AN INVESTIGATION OF ORGANO-COBALT COMPOUNDS

by

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PREFACE.

The work described in this thesis is presented for examination for the degree of Doctor of Philosophy of the University of Tasmania and was carried out during the two years, 1947-48.

The advice and encouragement of Professor E.E. Kurth, D.Sc. Professor of Chemistry, University of Tasmania is gratefully acknowledged. The work has been carried out under the general direction of Dr. J.B. Polya, Lecturer in Chemistry, University of Tasmania, whose enthusiasm and inspiration have been greatly appreciated.

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INTRODUCTION. GENERAL.

The work described in this thesis deals with the chemistry of cobalt and its compounds particularly the organic cobalt compounds. The main division of the work is into two sections Part A and Part B. This division has been made because while both sections discuss work relating to the organo-cobalt compounds there is a very definite difference in the nature of work discussed in the two sections as well as in the type of approach used and the results obtained.

In Part A the problem is concerned with the cobalt complex of 1-nitroso 2-naphthol. This problem is of course closely related with metallurgical practice in the production of zinc by electrolytic methods. The removal of cobalt from electrolyte solutions is essential if satisfactory deposition of the zinc is to occur. This removal of cobalt is usually carried out in acid solution by precipitation with 1-nitroso 2-naphthol. A red cobalt complex forms and this is filtered off. The filtrate containing the zinc can then be satisfactorily electrolysed. By igniting the red cobalt precipitate the organic material is removed and a residue of cobalt oxide obtained. This cobalt oxide is a valuable material and finds many applications commercially The process for obtaining this cobalt oxide has many disadvantages the most important being the loss of the organic material in the igniting process. This problem was thus

considered and some progress made towards its solution. It will be much better appreciated later how the emphasis in this work has been placed more on the immediate commercial requirements than the more fundamental aspects of the problem.

In Part B work dealing with efforts to prepare organo-cobalt compounds is considered. This work has been done in order to obtain a better idea of the fundamentals of cobalt chemistry, such as valence, electron distribution in various cobalt compounds etc., and with the hope too that any knowledge so gained might be of value in further research into the properties of the cobalt complex of 1-nitroso 2-naphthol. In this section a series of new compounds are described of the organo-cobalt type and a description of these compounds and some of their reactions is also included. It should be realised too that these studies have a value of their own in so far as cobalt and its various compounds are playing an ever increasing part in such fields as pharmacology, medicine, agriculture etc., and so any knowledge gained of an essentially basic and fundamental nature may affect in some measure studies in related fields. Attention has been placed in this section of the work on the theory and mechanism of various reactions with a view to obtaining fundamental information.

PART A

STUDY OF THE COBALT COMPLEX OF 1-NITROSO 2-NAPHTHOL

1. Introduction

Practically the whole of the literature of the 1-nitroso 2-naphthol cobalt complex[37] deals with the optimum conditions of precipitation and filtration and the influence of interfering metals. It is hardly necessary to present a full list of such references.[37,38,39] A few other references concern the nature of the bonding in the cobalt complex, but there is very little recorded information concerning the chemistry of this complex. Need for a better understanding of the chemistry of the cobalt complex of 1-nitroso 2-naphthol arises from two practical problems.[40] Careful experimental work indicates that when the cobalt complex is prepared by adding 2-naphthol, sodium nitrite and acid to a solution of cobalt the precipitate does not correspond to the theoretical compposition $CoC_{30}H_{18}N_3O_6$ but to one with a somewhat higher proportion of carbon to cobalt. This fact may be due to the absorption of 2-naphthol on the cobalt precipitate or absorption of 1-nitroso 2-naphthol, but other explanations are possible and the problem deserves careful consideration.

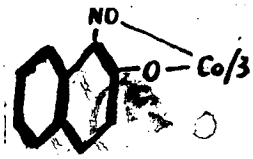
The second problem is of great economic importance. Precipitation of cobalt is carried out as has been mentioned to free the zinc solutions from cobalt and to obtain the latter in a convenient form. The organic reagent is lost in this process. Attempts to recover the organic reagent either

as the 1-nitroso 2-naphthol or as 2-naphthol or in some other convenient form were not successful when acids, caustic alkali or sulphides were used to split the cobalt complex. Treatment of the cobalt complex with sulphides gives some 1-amino 2-naphthol but the yields are very poor and isolation of the material is inconvenient. A suggestion was made to remove cobalt from its compounds by the action of carbon monoxide and nitrogen oxides (41) but attempts to use this method in the cleavage of the cobalt complex have been unsuccessful. The reduction of 1-nitroso 2-naphthol by sodium hydrosulphite has been studied by other authors and is included in Organic Syntheses (42) as a method of preparation of 1-amino 2-naphthol hydrochloride. The formation of 1-amino 2-naphthol-4-sulphonic acid has been noted on reducing 1-nitroso 2-naphthol in alkaline medium (43) but this reaction is not likely to proceed to any great extent since the yields of the 1-amino 2-naphthol hydrochloride are quite good. The application of this method to the cobalt complex of 1-nitroso 2-naphthol has been fairly successful and this work is reported later.

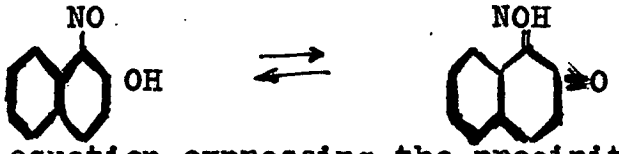
Some other facets of this problem have also been studied.

2. Nature of precipitation

Cobalt salts react with 1-nitroso 2-naphthol to precipitate a compound of the type



The 1-nitroso 2-naphthol may react either as the nitroso compound or as the oxime, these last two compounds being ordinarily in equilibrium.



The equation expressing the precipitation reaction may be formulated,

$$3\ C_{10}H_6\ (OH)(NO) + CoCl_2 \rightarrow C_{10}H_6\ (NO)(O)\ Co/3 + 2HCl + H.$$

It is apparent that hydrogen is formed in the reaction and it thus seems likely that a reducing reaction could proceed simultaneously with the above reaction. This conclusion may be expressed alternatively. Since the valency of cobalt changes from a divalency to a hexacovalency, i.e. since the cobalt is oxidised, some other constituent in the reaction may be reduced.

An experiment was designed to test this possibility.

A solution of 1-nitroso 2-naphthol was treated with an excess of cobalt sulphate under the usual analytical conditions.(15)

The precipitate was removed and the filtrate extracted with benzene and the benzene extract analysed. The extract consisted chiefly of acetic acid, and an unidentified organic material. This latter was found by extracting the benzene solution with aqueous sodium bicarbonate, acidifying this extract and treating with sulphuric ether. The material found was neither amino naphthol nor 1-nitroso 2-naphthol. As only a very small amount of this material was obtained no further attempts were made to identify it.

The conclusion was reached that the extent of any reducing reaction was so small as to be ignored when precipitation was carried out in the manner described.

3. Precipitants other than 1-nitroso 2-naphthol

The monoxime and dioxime of phenanthroquinone were prepared. The former may be used in a qualitative colour test for cobalt.(1) Experiments were carried out to explore quantitative possibilities of the test, but it was found that the resulting colour is a not too characteristic brown of insufficient intensity and considerably modified by the presence of interfering metals (copper, iron, nickel).

The absorption of cobalt by modified gelatin has also been attempted. Anionic gelatin was prepared by treating gelatin with 40% formaldehyde and isopropyl alcohol and cationic gelatin by acetylating gelatin with acetic anhydride.(2)

The results were unsatisfactory. The original paper does not indicate the best method of drying and our over-dried preparations turned into weak gels when passing aqueous solutions of cobalt through columns filled with modified gelatin.

4. Regeneration of the Organic Reagent from the 1-nitroso 2-naphthol cobalt complex

In view of previous failures to split the 1-nitroso 2-naphthol cobalt compled by acidic or basic action alone it was decided that methods of reduction may be more appropriate. Hydrogen sulphide, a mild reducing agent, was without effect. Nascent hydrogen, obtained from sodium and alcohol did not remove cobalt. Some action, however, took place as the alcoholic solution of the cobalt complex darkened. This dark material could not be cleared with hydrochloric or nitric acids in alcohol solution, but hydrogen sulphide precipitated cobalt sulphide from the alcoholic solution of the dark material. The organic residue was heterogeneous. Further purification, mainly removal of sodium ethoxide, gave a small amount of an acid substance, free from nitrogen and not identical with 2-naphthol. Partially hydrogenated 1-naphthol could have been formed under the experimental conditions. Owing to difficulties in separating possible stereoisomers no more work was carried out on the residue. Oxalic acid also

precipitates cobalt oxalate from the cobalt complex reduced with sodium and alcohol. In this case also recovery of the organic residue is difficult because of poor yields and the presence of a complicated mixture of byproducts. Owing to the expensive and dangerous nature of sodium it was decided not to concentrate attention on these experiments unless all other methods failed. Sodium sulphite and sodium bisulphite were tried without success.

It is known that sodium hydrosulphite reduces 1-nitroso 2-naphthol to the 1-amino 2-naphthol in good yields (42) and so this method of reduction was applied to the cobalt complex. The cobalt was precipitated almost quantitatively as cobalt sulphide and acidification gave good yields of 1-amino 2-naphthol hydrochloride. This material was identified by preparation of the benzoyl derivative m.p. 235° and also by oxidation with ferric chloride to the 1,2-naphthoquinone m.p. 145°. Oxidation of the 1-amino 2-naphthol with ferric chloride gave 1,2 naphthoquinone, m.p. 145°, to the extent of 92-94% theory. Treatment of this naphthoquinone with hydroxylamine hydrochloride in alcohol solution gave 2-nitroso 1-naphthol m.p. 152° Corr. 152°. Yield of 2-nitroso 1-naphthol 90% theory.

The 2-nitroso 1-naphthol will also precipitate cobalt giving 100% precipitation and this complex may also be

reduced with sodium hydrosulphite giving 2-amino 1-naphthol which may again be oxidised to 1, 2 naphthoquinone with ferric chloride. The yield of 2-amine 1-naphthol hydrochloride from the reduction of 8 grams of the cobalt complex of 2-nitroso 1-naphthol with sodium hydrosulphite was 2.3 grams or 26% of the theoretical amount. It is probable however that a study of the optimum conditions for the reduction would enable greatly increased yields.

Either the cobalt complex of 1-nitroso 2-naphthol or 2-nitroso 1-naphthol may be broken down with hydrosulphite to amino naphthols and so the chief problem now appears to be to conversion of 1-amino 2-naphthol or 2-amino 1-naphthol to cobalt precipitating material, preferably nitroso naphthol. The use of hydroxylamine as outlined above is prohibited by cost. The high cost of 2-nitroso 1-naphthol (approximately 4 times that of 1-nitroso 2-naphthol) which may be obtained from 1, 2, naphthoquinone is noteworthy.

Attempts have been made to oxidise 1-amino 2-naphthol to 1-nitroso 2-naphthol. The reagents used and products isolated are listed below.

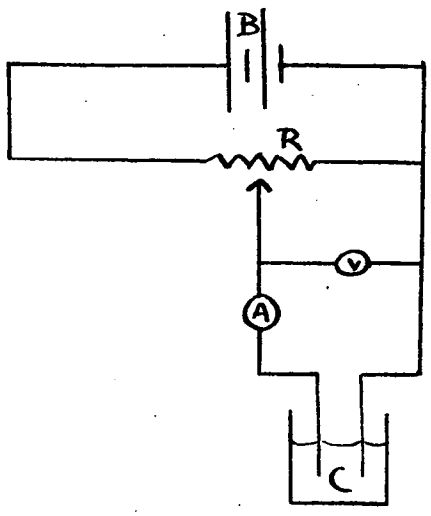
Material oxidised	Oxidiser	Product
1-amino 2-naphthol	Ferric chloride (44)	1,2,naphthoquinone
	Potassium persulphate, (45)	"
	Chromic acid	"
	Peracetic acid	"

Despite the consistent production of the naphthoquinone it was thought that some study of the oxidation reaction mechanism might yield information so that the oxidation could be guided to the 1-nitroso 2-naphthol compound. This study of the reaction mechanism has been begun by using the technique of electrolytic oxidation.

Only a few preliminary experiments have so far been performed but even these give some indication that the oxidation of amino naphthol to nitroso naphthol is possible.

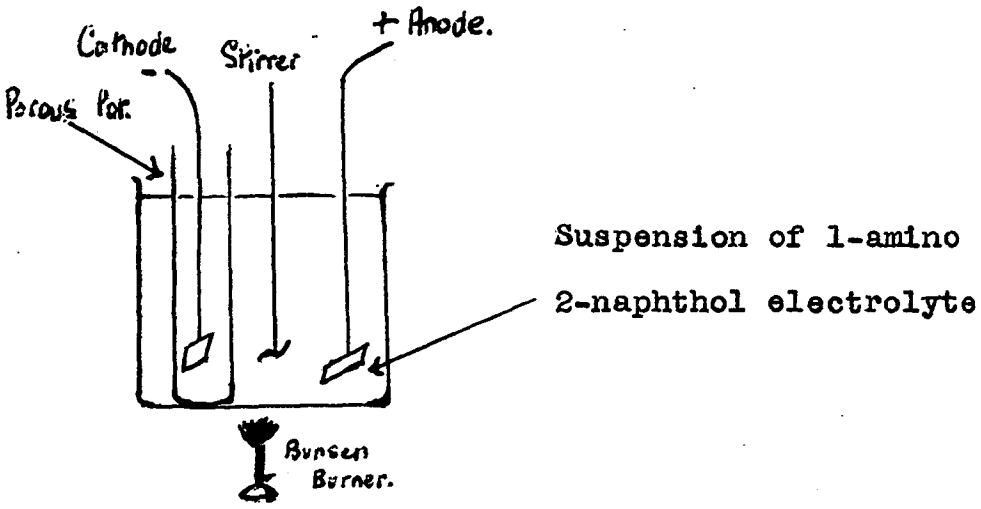
5. Electrolytic oxidation of 1-amino 2-naphthol

The type of electrical set up used in these oxidation experiments is sketched below.



B	4 volt batteries
R	Rheostat 50
V	Voltameter
A	Ammeter
C	Cell

The actual cell used is drawn in more detail below



Electrolyte	Various solutions were used to suspend the amino naphthol, e.g. water, 20% sulphuric acid, 50% glacial acetic. Water and acetic acid were found most satisfactory.
Cathode	A platinum cathode was used in all experiments.
Anode	Platinum, lead and carbon were all used, carbon being found very satisfactory.
Catalyst	Chromic sulphate was tried but did not appear to influence results over much.
Potential	A potential of about 3 volts was used.
Current Density	This factor varied in different experiments from 0.01 - 0.25 amps./om^2.

Temperature — A temperature of approximately 80 - 90°C was maintained to cause maximum solubility of the 1-amino 2-naphthol with minimum evaporation of solvent.

Time — An arbitrary time value of 12 hours for oxidation seemed satisfactory.

Concentration of 1-amino 2-naphthol

A concentration of approximately 4 grams of the amino naphthol was used in 2 litres of solution.

Results

It was hoped that the oxidation would proceed by way of the 1-nitroso 2-naphthol and cobalt was accordingly added to the solution so that if the nitroso-naphthol was formed it would be stabilised by formation of its cobalt complex. After the oxidation appeared complete the residue was filtered off. This residue was brown in colour and after washing to remove all absorbed cobalt salts the residue was tested for the presence of cobalt. Only small amounts of cobalt were however found and it is doubtful if any of the 1-nitroso 2-naphthol is formed in the oxidation. The residue seemed to consist mainly of 1,2 naphthoquinone since treatment of the residue with

hydroxlamine gave a material which would precipitate cobalt. This treatment of course would convert the naphthoquinone to 2-nitroso 1-naphthol.

A great deal more work is necessary to establish the nature of the oxidation process and to determine whether 1-nitroso 2-naphthol is formed as an intermediate or whether this compound may not be formed under certain special conditions.

Since the oxidation is apparently accomplished so easily and since 1,2 naphthoquinone is the main product it is probable that gentle oxidising conditions utilising low overpotential and low current densities may be more likely to yield the nitroso compound.

Summary and Conclusions

1) The cobalt complex of 1-nitroso 2-naphthol is very resistant to attack but reduction with sodium hydrosulphite in alkaline solution breaks the complex into 1-amino 2-naphthol and cobalt sulphide.

2) The conversion of the 1-amino 2-naphthol to cobalt precipitating material may be accomplished by oxidising to the 1,2 naphthoquinone and then treating this quinone with hydroxylamine. In this way 2-nitroso 1-naphthol is formed and this material precipitates cobalt satisfactorily.

However commercial applications demand that some simpler and cheaper method be formulated for the reconversion of the amino naphthol to nitroso naphthol.

3) Electrolytic oxidation seems to offer hope of a reasonable method for the preparation of 1-nitroso 2-naphthol from 1-amino 2-naphthol. Preliminary experiments in this direction have been carried out but so far with little success.

4) Other methods of precipitating cobalt have been found unsatisfactory.

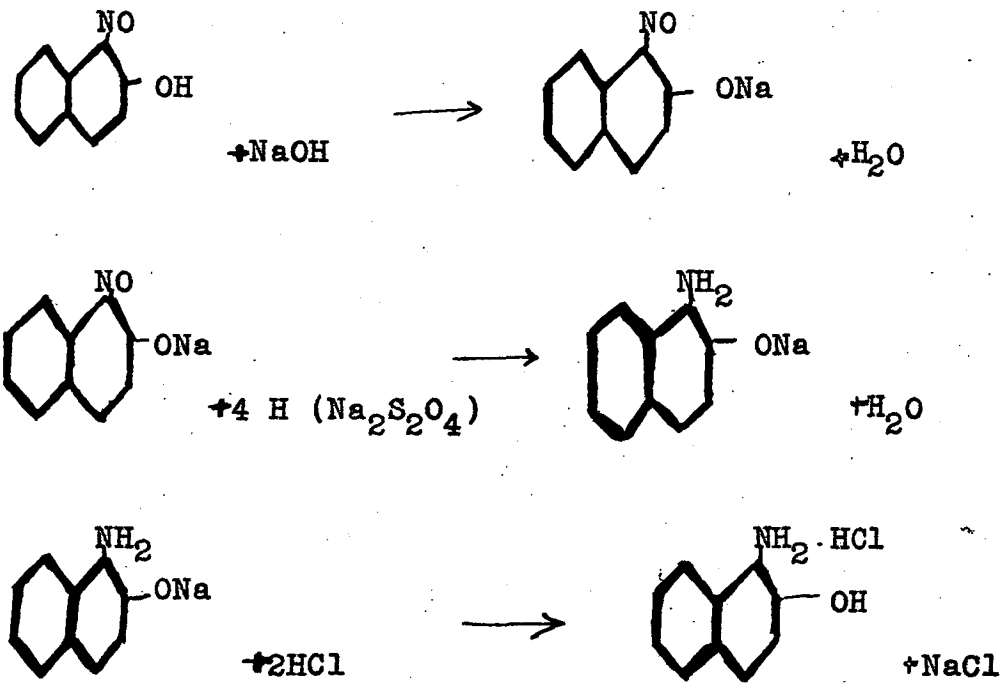
7. Experimental

1-nitroso 2-naphthol. (Org. Syn. Coll. Vol.I, 1941, 411)

In a 12 litre flask with a mechanical stirrer 500 g. of technical b-naphthol were dissolved in a warm solution of 140 g. of sodium hydroxide in 6 litres of water. The solution was cooled to 0°C in an ice bath and 250 g. of powdered technical sodium nitrite was added. With stirring, 1100 g. of sulphuric acid (Sp.gr. 1.32) was added over a period of 1.5 hours and so that the temperature was maintained at 0° crushed ice was added to keep the temperature at 0°C. After all the acid was added the solution reacted acid to Congo Red paper. The mixture was stirred for one hour and then the 1-nitroso 2-naphthol which separated out during the reaction was filtered off and thoroughly washed with water.

After air drying the product weighed 665 grams or 99% theory. This material melted at 97°C.

1-amino 2-naphthol hydrochloride



In a 2 gal.crock with stirrer were placed 240 g. a-nitroso-b-naphthol and 300 cc. 5 N NaOH. The lumps were broken and the mixture stirred for 30 minutes. The bulk of the nitroso compound thus dissolved and 1200 mls. 5 N NaOH were added. Steam was passed in until the temperature was 35° and then 600 g. sodium hydrosulphite (at least 85% pure) was added while the solution stirred. The temperature rises to 60-65°C and the solution was then stirred for one minute at five minute intervals during a half hour.

The solution was cooled to 20° by the addition of ice and 500 mls. HCl were added. The precipitate of amino naphthol was collected and pressed free of liquor and placed in a crock with 2.5 l. water and 250 mls. HCl. The solution was heated to 85-90°C with steam and held for 1 hour at this temperature. The hot solution was cooled and filtered, the filtrate being poured into 1200 cc. of conc. HCl. The amino naphthol began to precipitate immediately. The hydrochloride was collected and washed with HCl and ether. Then the product was air dried.

Yield 180 grams or 65% theory.

Reduction of the cobalt complex of 1-nitroso 2-naphthol

24 grams of the cobalt complex was suspended in 150 mls. of water and 30 mls. of 5N NaOH and stirred for 30 minutes so that the complex was thoroughly broken up. 120 mls. of the 5N NaOH was then added and the mixture heated with steam to 35°C. 60 grams of sodium hydrosulphite (85% pure) was then added when the temperature rose to about 70°. After standing for two hours the mixture was acidified when a white flocculent precipitate of 1-amino 2-naphthol formed. This was filtered off and dissolved in hot water and then recrystallised from concentrated hydrochloric acid as in the preparation of the amino naphthol from 1-nitroso 2-naphthol. The filtrate was found to contain cobalt chloride.

Yield of 1-amino 2-naphthol 9,8 grams or 51% theory.

The filtrate in this experiment was made up to 1 litre and a portion of 50 mls. analysed for cobalt with 1-nitroso 2-naphthol. 92% of the cobalt in the original complex was thus recovered.

Oxidation of 1-amino 2-naphthol with ferric chloride

The oxidising solution was made by dissolving 240 g. of ferric chloride hexahydrate in a mixture of 90 mls. of concentrated hydrochloric acid and 200 mls. of water with heating, cooling to room temperature with ice, and filtering with suction. 80 grams of 1-amino 2-naphthol was placed in a flask and covered with a solution of hydrochloric acid (5 cc.) in 3 litres of water heated to 35°. The material was dissolved quickly, filtered rapidly, and the oxidising solution added rapidly so that complete mixing of the two solutions occurs almost instantaneously. The 1,2 naphthoquinone separated almost immediately as a voluminous yellow precipitate. The precipitate was filtered and well washed with water and then dried on filter paper at room temperatures. The material is golden yellow colour and melts with decomposition at 145°. Yield 60 grams or 93% theory.

Preparation of 2-nitroso 1-naphthol

1,2 naphthoquinone 10 g. was dissolved in alcohol and heated with an alcoholic solution of hydroxylamine hydrochloride

an excess of this latter material being used. The product of the reaction was precipitated with water, filtered and washed with water. Yield of 2-nitroso 1-naphthol 10 grams or 90% theory. m.p. of the 2-nitroso 1-naphthol 152°.

Preparation of phenanthraquinone

A solution of 2.2 parts of chromic oxide in 5.6 parts of warm glacial acetic acid was added to one part of phenanthrene in 4 parts of glacial acetic acid. The oxidation was completed by refluxing for about 30 minutes. Most of the solvent was recovered by distillation and the residue was then poured into water. The precipitate thus obtained was washed with alkali and water and then stirred with sodium bisulphite. The phenanthraquinone was recovered from the bisulphite solution by adding acid and purified by crystallisation from alcohol. m.p. 205°. 5 grams of phenanthrene gave 1.5 grams of the quinone, corresponding to a yield of 26% theory.

Phenanthraquinone monoxime

1 gram of phenanthraquinone was treated in 15 mls. of ethenol and 5 mls. of chloroform with 0.5 gram of hydroxylamine hydrochloride by boiling for 1 hour. The solvent was removed and the monoxime recrystallised from ethanol. Yield of phenanthraquinone monoxime 0.6 gram or 60% theory. The product melted at 157°. Corr. 158°.

Phenanthraquinone dioxime

1 gram of phenanthraquinone was refluxed with 2 grams of hydroxyl-amine hydrochloride and 2 grams of barium carbonate in 50 mls. of alcohol. The solvent was removed, after filtration to remove excess barium carbonate, and the dioxime of phenanthraquinone recrystallised from hot ethanol. M.p. 202°. Yield 0.4 gram or 40% theory.

Electrolytic Oxidation

Experiment 1

Electrolyte	20% H_2SO_4
Catalyst	2% chromic sulphate
Temperature	90-100°C.
Potential	3v.
Current Density	0.25 amp./sq.cm.
Electrodes	Anode: Lead. Cathode: Platinum
Time of oxidation	12 hours

Concentration of 1-amino 2-naphthol... 35 grams/2 litres

Product. 1,2 naphthoquinone. No 1-nitroso 2-naphthol.

Experiment 2

Electrolyte 4.2 grams 1-amino 2-naphthol hydrochloride and 8 grams cobalt chloride (cryst.) in 2 litres of water.

Temp. 90-100°

Time. 12 hours

Carbon anode; platinum cathode

Current density. 0.05 amp/sq.cm.

Voltage. 4 v.

Product. 1,2 naphthoquinone. Trace of cobalt.

Experiment 3

Electrolyte, 0.3 gram 1-amino 2-naphthol and 0.14 gram of cobalt chloride in 2 litres of water.

Carbon anode; platinum cathode.

Current density. 0.01 amp/sq.cm.

Time of oxidation. 15 hours

No cobalt found in residue which consisted mainly of the 1,2 naphthoquinone.

Experiment 4

Electrolyte. 2 litres of 30% glacial acetic acid (by volume) 5 grams 1-amino 2-naphthol; 10 grams cobalt chloride.

Carbon anode; platinum cathode

Current density. 0.1 amp/sq.cm.

Small amount of cobalt found in the residue but the residue was mainly the 1,2 naphthoquinone.

PART B

ORGANIC COBALT COMPOUNDS

1. Introduction.
2. Direct cobaltation.
3. Decomposition of cobalt sulphinate.
4. Decomposition of diphenyl iodonium iodide.
5. Decomposition of aromatic diazonium compounds.
6. Decomposition of phenyl diazonium cobaltinitrite.
7. Reaction of the Grignard reagents with cobalt halides.
8. Summary and conclusions.

PART B

ORGANO-COBALT COMPOUNDS

1. Introduction

As has been mentioned (See General Introduction) this study of the methods available for the preparation of organo-cobalt compounds was begun because such a study seemed most likely to yield information of value in the understanding of the fundamental properties of cobalt in its compounds and in its reactions. The term organo-cobalt is of course a very broad one and in this discussion it is not proposed to include in the term, co-ordination compounds of cobalt with organic and inorganic compounds, or cobalt cyanides and carbonyls. Some discussion of the last of these will however be included in later discussions. The term organo-cobalt compound will be restricted to those compounds of cobalt in which the cobalt is linked to a hydrocarbon type of molecule, with a carbon to cobalt linkage.

The problem of the preparation of an organo-cobalt type of compound falls under the general heading of organo metallic compounds. These latter may be broadly defined as compounds which have a direct union of carbon with a metal. (3) The first organo metallic compound was prepared by Frankland in 1849. He tried to prepare the ethyl radicle from ethyl

iodide and zinc but obtained instead diethyl zinc.

There are many methods available for the preparation of organo metallic compounds and according to Gilman[4] the main general methods may be indicated as below.

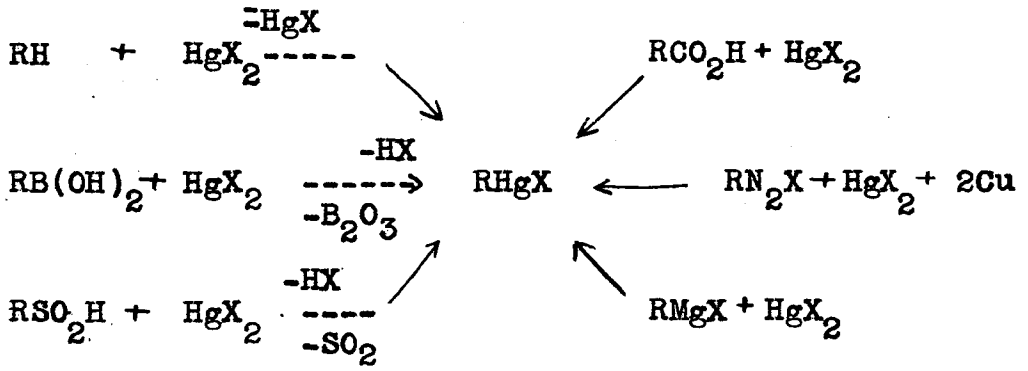
$RX + M \rightarrow RMX$ or $2RX + M \rightarrow R_2M + MX_2$ 1.

$R_2M' + M'' \rightarrow R_2M'' + M'$ (M'' higher potential than M') 2.

$R_2M' + M''X_2 \rightarrow R_2M'' + M'X$ (M'' lower potential than M') 3.

We thus have interaction of an RX type of compound with a metal, alloy or amalgam. These three types of reaction may be easily represented with examples. Thus for Reaction 1 we have the well known Grignard reaction and also the preparation of organo zinc and lithium compounds. The latter two compounds are most effective in the type of transformation shown in reactions 2 and 3. Lithium reacts with RMgX in accordance with reaction 2; and organo-aluminium compounds are formed from the Grignard reagent and aluminium chloride in accordance with reaction 3. In general reaction 2 yields a more reactive compound from one that is less reactive while the reverse is the case in reaction 3.

It was hoped that the close resemblance of cobalt to magnesium might indicate that methods successful with magnesium would be equally successful in the case of cobalt. Organomercurials may be prepared as follows:



Thus these methods were attempted with suitable modifications to prepare organo-cobalt compounds.

2. Direct cobaltation

Organo-mercury compounds can be made by refluxing mercury salts with hydrocarbons.[30,31] Similar experiments with cobalt salts have been unsuccessful.

Cobaltation was attempted with cobalt acetate which had been dehydrated in a Dean Stark trap. Benzene derivatives were used as it was thought that the substituents would enable some reaction mechanism to be formulated if the reaction were successful. The procedure used was simple and consisted of heating anhydrous cobalt salts under reflux with hydrocarbons such as toluene for 1 or 2 hours. The mixture was then filtered and the solvent removed under reduced pressure. Sometimes the solvent was washed with water before the vacuum distillation and it should be noted that even where this process of washing was included no cobalt hydroxide was ever found. Had any cobalt hydroxide been

found of course this could have been regarded as positive evidence for the existence of an unstable organo-cobalt compound.

Benzene and phenol and nitrobenzene all gave negative results. Toluene was found to contain considerable quantities of aluminium chloride and removal of this material was very difficult. When toluene was used in these experiments a small amount of residue was obtained which contained cobalt. When the toluene was purified however this residue was not found after the distillation. The results of these experiments were thus all negative, but it is possible that aromatic ethers would metalate more readily and perhaps form organo-cobalt compounds.

A brief resumé of the experiments carried out in this section are set out below.

Experiment 1

250 mls. of toluene were refluxed with excess cobalt acetate for two hours. No cobalt was found on removal of the solvent under reduced pressure.

Experiment 2

250 mls. of purified toluene were refluxed with excess cobalt acetate for 2 hours. 25 mls. of ethanol were added to the reaction mixture to remove any acids formed. The

solvent was removed under reduced pressure but no organo-cobalt compounds were found.

Experiment 3

200 mls. of nitro benzene and 5 grams of phenol were refluxed with 8 grams of cobalt acetate for 1 hour. Removal of the solvent, nitrobenzene, did not leave any cobalt residue.

Experiment 4

5 mls. of furfural and 8 grams of mercuric acetate were refluxed with 2.5 grams of sodium acetate to form the organo-mercury compound. 5 grams of cobalt acetate were added to the reaction mixture to test the possibility of replacement of the mercury by cobalt. Ethanol was used as a solvent and removal of this solvent gave a residue which was extracted with water. After the wash with water no cobalt was left in the residue and so no replacement could have occurred.

Other experiments similar in method to those outlined above were tried varying amounts of alcohols such as methanol, ethanol and propanol being added so that any acids formed in the reaction would be removed. However even when this precaution was taken no cobalt was found in the residues.

Purification of toluene

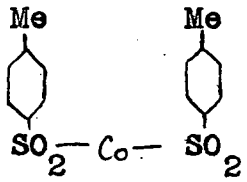
Considerable amounts of aluminium chloride were found in the toluene used in the cobaltation experiments and this was removed as follows:-

500 mls. of toluene were refluxed with concentrated sulphuric acid and then extracted four times with sulphuric acid. Washing with portions of caustic soda (40%), in all some 200 mls., and then finally washing with water removed most of the aluminium chloride. The toluene was finally dried over calcium chloride and distilled first at atmospheric pressure and then under reduced pressure.

3. Decomposition of cobalt sulphinate

p-toluene sulphinate was converted by the method of Whitmore and Hamilton (32) into sodium p-toluene sulphinate. The recrystallised product was dissolved in hot water and a concentrated solution of cobalt chloride added with good stirring. Pink cobalt sulphinate separated out. This compound was free from halogen and insoluble in alcohol, ether, acetone, chloroform and benzene but soluble in pyridine. On heating the pyridine solution a blue colour developed. A similar effect was obtained by heating the compound with aromatic ethers like anisole, phenetole or safrole. Acids decolourised the compound and hydrochloric acid gave cobalt chloride and p-toluenesulphonyl chloride.

The compound may be formulated as

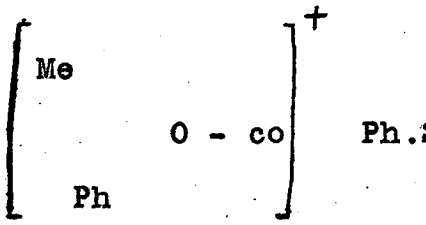


$= (p\text{-}Me\text{-}C_6H_4\text{-}SO_2)_2Co$

Attempts were now made to decompose this compound in such a way that sulphur dioxide would be removed and there would be a linkage formed between the aromatic part and the cobalt. The compound was thus heated both in the air and in the vacuum. The decomposition was essentially similar in both cases. The changes which occurred on heating are indicated below:-

Temperature	Change observed
40°	Blue colour appeared.
160°	The whole mass was blue and some slight evolution of gas was seen.
250°	At this temperature the whole mass fused, and white crystals of a sulphone or polysulphone sublimed. More gas, sulphur dioxide, was given off and the mass fused.
290°	The whole mass was black and no further changes occurred up to 340°.

Thus it was evident that considerable decomposition of the sulphinate had occurred. The heated mass was extracted with various solvents leaving cobalt oxide as a residue. Alcohol dissolved cobalt sulphate with a blue colour. Ether extracted white crystals which seemed to be a mixture of sulphones and polysulphones and these white crystals were soluble in benzene. Sulphur dioxide was evolved during the heating. Addition of traces of mercury, copper or a mixture of mercury and copper, had no catalytic effect. Owing to the protective influence of sulphur dioxide oxidation cannot occur to any great extent during the reaction yet the bulk of the cobalt is converted to cobalt oxide. If the organo-cobalt compound is formed at all then it must be very sensitive to heat. The blue colour formed on heating with ethers may indicate the formation of oxonium compounds.



$Ph.SO_2^-$. Co: co-ordinative equivalent of cobalt.

The blue colour disappears on standing or on dilution.

It thus appears that the decomposition of the cobalt sulphinate will not afford the organo-cobalt compounds and these experiments were abandoned.

4. Decomposition of Diphenyl iodonium iodide

Markarova and Nesmayanov[19] reported that organo mercury compounds could be prepared by treating diphenyl iodonium iodide in propanol solution with mercury.
In attempts to prepare organo-cobalt compounds therefore diphenyl iodonium iodide was prepared and treated with iron cobalt and nickel powders in propanol solution. The metal powders were made by heating the metal oxalates in an atmosphere of hydrogen in a long glass tube. The solution of diphenyl iodonium iodide was heated with the metal powders under reflux for 5 hours. In the three cases tried a reaction was observed to occur. Thus the solutions using iron cobalt and nickel became respectively brown, blue green and yellow green. Finally after heating had been carried out for 5 hours the iodide was all in solution and the reaction was judged completed. The mixture was filtered to remove excess metal powders and then the solvent was removed by distillation under reduced pressure. In all cases a residue was left. This residue was examined and found to consist of unchanged diphenyl iodonium iodide, the metal halide, i.e. iron cobalt and nickel iodides, free iodine and some phenyl iodide, with some diphenyl. Thus in these experiments reaction appears to lead not to the organo metallic compound but to biradicals.

The formation of this last material, biphenyl, could be accounted for by postulating some intermediate of the organo cobalt type. Experiments using naphthyl iodonium iodides might yield the required organo cobalt compounds.

Three typical experiments using iron cobalt and nickel powders are described below.

Quantities of materials used	Iron	Cobalt	Nickel
Wt. metal powder	0.92	0.46	1.1
Wt. diphenyl iodonium iodide	1.8	0.92	2.2

Volume of solvent propanol 50 mls.

The above quantities were used in three typical experiments and the mixtures were heated during 5 hours under reflux.

Similar experiments to these were carried out using larger amounts of cobalt powder and also using cobalt salts, cobalt acetate, and chloride but in no cases could any organo-cobalt compounds be found.

Experiment

$Ph_2$1.1, 0.7 grams, 2.0 grams cobalt powder, prepared by treating a cobalt aluminium alloy with strong caustic soda, were heated in anisole solvent. Again however no organo-cobalt compound found.

5. Decomposition of diazonium compounds

The decomposition of diazonium compounds has been often used to prepare organo-metallic compounds.[23,16,17] Generally the aromatic diazonium compound is treated directly with a metal powder when decomposition occurs. Reaction is usually effected in acetone solution. Chalk is sometimes added to remove acids formed during the decomposition. The theory of the decomposition of aromatic diazonium compounds has been thoroughly studied by Waters and co-workers.[16,17] They have shown that in the reactions between neutral acetone solutions of diazonium chlorides and some chemical elements such as mercury, antimony and tellurium the decomposition is non-ionic and involves isomerism of the diazo salt to the covalent diazo chloride $(PhN_2)\,Cl \rightarrow Ph.N{:}\,NCl$ followed by decomposition of the latter to nitrogen and neutral radicles

$$Ph.\,N{:}\,NCl \longrightarrow Ph. + N_2 + Cl.$$

The reaction between a free radicle and an atom is an addition process

a) $Ph. + {}^{\cdot}\dot{\underset{\cdot\cdot}{Hg}}{}^{\cdot} + Cl. \rightarrow Ph{:}\,Hg{:}\,Cl$

b) $2Ph. + .\dot{\underset{\cdot\cdot}{Se}}. \longrightarrow Ph{:}\,\dot{\underset{\cdot\cdot}{Se}}{:}\,Ph$

for the electrons in atoms other than those of zero valency tend not to pair with one another but to occupy different orbitals keeping their spins parallel. Thus stable bonding

pairs can be formed by union of odd electrons of free radicles with unpaired electrons of the metal atoms.

Waters (16) found that the decomposition of phenyl magnesium chloride in acetone with iron, cobalt and nickel powders gave diphenyl and phenyl chloride but no organo-metal compounds

Experiments have been carried out using naphthyl diazonium compounds as it was thought that these compounds might give rise to stable organo-cobalt compounds. Reactions were made in acetone solutions sometimes with chalk to ensure a neutral solution. Efforts were also made to secure the addition compounds of cobalt salts with diazonium compounds but these addition compounds were generally formed in such poor yields that this method was abandoned.

The usual technique was very simple. The diazonium compound was formed and decomposed in acetone solution. After the cobalt powder had been added or in some instances copper powder and the decomposition effected, the acetone was removed under reduced pressure and the residue washed with water and then examined for cobalt. No cobalt was found in the residue from any experiment and these experiments were all thus unsuccessful in the preparation of an organo-cobalt compound.

A brief account of these experiments is given below.

EXPERIMENTAL

Experiment 1.

a-naphthyl amine (1 mol.) was diazotised in concentrated hydrochloric acid and a solution of cobalt chloride (130 grams) in hydrochloric acid added. Small amounts of a black addition compound formed and this was filtered off and dissolved immediately in acetone. The solution in acetone was treated with 1 gram of copper powder and left overnight. The mixture was filtered and the residue obtained by removal of the acetone under vacuum, washed with water. The residue contained no cobalt.

Experiment 2

The above experiment was repeated using 0.2 molar quantities but again the experiment was unsuccessful.

Experiment 3

Aniline (100 grams) was diazotised and 120 grams of cobalt acetate dissolved in concentrated hydrochloric acid was added. Small amounts of a black addition compound formed and this was filtered off and dissolved in acetone. 3 grams of copper powder was added to decompose the addition compound and the mixture stood overnight. Removal of the acetone left a black residue, and some of this residue was soluble in alcohol.

Water precipitated a blue compound which contained copper and halogen and was also partly organic. The material contained 41.1% copper. Unfortunately only 0.1 gram of this material was obtained and further analyses were impossible. The compound was blue in colour and hydrolysed by hot water and alkalis. With caustic soda a blue material formed and this was insoluble in alcohol but soluble in acids and was probably copper hydroxide. When the blue compound was heated a residue remained and this was found to be copper oxide. The compound thus appeared to be an organo-copper compound and furthermore one containing halogen. However the yield of this compound was so low as to make the preparation of the compound exceedingly difficult.

Experiment 4

10 grams of phenylamine was converted to the solid diazonium chloride and isolated as a white compound by the method of Kipping and Kipping (33) using acetic acid and amyl nitrite. The final diazonium chloride was precipitated with ether. This solid diazonium salt was dissolved in acetone containing cobalt chloride. A change in colour was observed which indicated that some reaction was proceeding. No cobalt could be found in the residue remaining after the acetone was removed.

Experiment 5

10 grams of PhN_2Cl in an acetone neutral with chalk were treated with copper powder. Decomposition of 10 grams of PhN_2Cl in acetone without chalk was also effected with copper powder. A third experiment in which 10 grams of PhN_2Cl were decomposed with copper powder in acetone containing 10 grams of anhydrous cobalt chloride was also made. In all these experiments however the residue remaining after removal of the solvent contained no cobalt.

Experiment 6

a- and b-naphthyl amines (10 grams) were diazotised with sodium nitrite in a solution of glacial acetic acid and hydrochloric acid. The solid diazonium salts were precipitated with ether. The yields of solid diazonium salts were poor being about 40% theory. The salts were dissolved in 100 mls. of dry acetone with 10 grams of chalk and 4 grams of cobalt powder. A reaction occurred and after standing overnight the acetone was removed. The residue was black and tarry and water removed pink cobalt chloride. Some polymeric forms of naphthalene were also found in the residue but these contained no cobalt and were not examined further.

Method used in the diazotisation of the aromatic amines

Aniline is used here as an example but corresponding quantities of the naphthyl amines may be easily substituted.

Aniline (100 grams) was dissolved in 100 mls. of water and 480 mls. of concentrated hydrochloric acid. The mixture was cooled to about 5°C by the addition of ice (1 Kg.). 78 grams of sodium nitrite was then added as a solution in 500 mls. of water. This mixture was stirred during the addition of the sodium nitrite and ice was added to keep the mixture at 5°. Completion of the diazotisation was shown with starch iodide paper. To form the addition compound of the diazonium salt with cobalt chloride, 120 grams of cobalt chloride in 100 mls. of concentrated hydrochloric acid were added. Small amounts of a black solid formed and this was filtered off.

Preparation of solid diazonium salts

8 grams of a- or b-naphthylamine were suspended in glacial acetic acid (20 grams) and concentrated hydrochloric acid (7 grams). The mixture was cooled to 5°C by placing the reaction flask in ice salt mixture. 7 grams of solid sodium nitrite was added and after standing for 30 minutes to complete the reaction, ether was added when precipitation of the solid naphthyl diazonium chloride occurred. This material was immediately filtered and used as decomposition of the material is very rapid.

6. Decomposition of phenyl diazonium cobaltinitrite

Hodgson and Marsden[18] prepared a compound $(C_6H_5N_2)_3Co(NO(NO_2)_6$ by diazotising aniline, neutralising with chalk,

filtering, and adding sodium cobaltinitrite. They found the pale yellow solid which formed to have the formula shown above. By decomposing the compound in aqueous media with sodium nitrite, copper sulphate and cuprous oxide they obtained nitro benzene.

It was thought that if the compound were decomposed in organic solvents the decomposition might yield an organo cobalt compound. The cobaltinitrite compound was therefore prepared.

Decomposition was effected in acetone solution in the presence of copper powder. The acetone was removed and the residue examined. After thorough washing with water the residue which remained was soluble in alcohol and thus some organo-copper compound was formed. This was not investigated.

Decomposition was next carried out in acetone without copper being present. Heat was necessary to start the decomposition but once started the reaction was exothermic. Examination of the products of the reaction showed only cobalt nitrate and nitro benzene.

These experiments did not thus yield any organo cobalt compounds. There is some possibility of success with the corresponding naphthalene compounds.

Only qualitative experiments were made in this section of the work and as positive results indicating the formation of organo-cobalt compounds were not obtained these experiments were not pursued further.

7. Reaction of the Grignard reagents with cobalt halides

(a) Introduction.

(b) Preliminary or exploratory experiments.

(c) Reaction of the a- and b-naphthalene series.

(d) Reaction with other alkyl and aryl groups.

(e) Reaction with some other Group VIII elements.

(f) Properties and reactions of the organo-cobalt compounds.

(g) General theory.

(h) Summary and conclusions.

(j) Experimental methods.

(a) Introduction

The Grignard reagents are the most widely used materials for the preparation of organo-metallics and these materials are the most important among organo-metallic compounds. Their success in the preparation of other organo-metallic compounds may be due to the fact that the Grignard reagents already possess a carbon-metal linkage whereas methods of preparation involving the formation of free radicles or the decomposition of complex unstable materials are more likely to result in radicle coupling than in the formation of new compounds.

The Grignard reagent has been used to prepare organo-copper, silver and gold compounds.[24,25,26] Also the organo compounds of gallium, indium and thallium have been prepared by interaction of the metal halides with the Grignard reagent.[27,28,29] Interaction of the metal halides with organo-lithium compounds also is successful in these last three cases.

The studies of Hein[12] resulting in the preparation of organo-chromium compounds also give evidence of the usefulness of the Grignard reagents in the preparation of other organo-metallics.

In many cases the reaction with the Grignard reagent and a metal halide leads to the formation of coupling products.

$$2RMgX + Cu_2Cl_2 \longrightarrow 2RCu \longrightarrow R\text{-}R + 2Cu$$

This type of reaction has also been observed in the reactions of the Group VIII metal halides.[7, 20] In all these cases the intermediate organo-metallic has been postulated as an unstable intermediate.

(b) Preliminary and exploratory experiments

In discussing the experiments and results in this section it is proposed to follow as closely as possible the order in which the experiments were actually carried out as this should enable a logical sequence to be maintained. Only enough discussion of the experiments will be included

at first to enable a complete picture to be obtained and detailed discussion of results and theories will be left until later.

The first experiments involved the use of high boiling solvents such as anisole and pyridine instead of the usual ether. It was thus hoped that the higher temperatures would permit reaction between aromatic halides and cobalt metal. These experiments are outlined briefly below.

Experiment 1

40 mls. pyridine; 10 mls. phenyl bromide; 20 grams pyrophoric cobalt powder were refluxed for 2-3 hours. No reaction could be seen to have occurred.

Experiment 2

20 mls. anisole; 20 mls. phenyl bromide; 2 grams cobalt chloride (anhydrous) were refluxed for two hours but again no reaction could be seen to have occurred.

Experiment 3

20 mls. anisole; 20 mls. phenyl bromide; 2 grams pyrophoric cobalt powder were refluxed for 2 hours but no visible reaction occurred. In the experiments shown above the solvents were in all cases removed by distillation in vacuum after the reaction was completed but no residues were obtained in any case.

In the next experiment ethyl magnesium iodide was formed and treated with cobalt chloride (anhydrous). A reaction occurred, heat was formed, and by pouring the reaction product into water cobaltous hydroxide was found. It thus appeared that an organo-cobalt compound had formed and that it was furthermore decomposed by water. In the reaction 4 grams magnesium were used with 20 grams ethyl iodide in 20 mls. ether to form the Grignard reagent and to this ethereal solution was then added 4 grams of solid anhydrous cobalt chloride. The mixture was stood overnight.

This experiment was not immediately pursued further but since some indication of a positive reaction had been obtained an experiment was designed using α-naphthyl iodide instead of ethyl iodide. An ethereal solution of α-naphthyl magnesium iodide was made as below. α-Naphthyl iodide (10 grams), magnesium (1 gram) were heated together in 30 mls. of very dry ether. To the solution of the Grignard reagent was added excess of solid anhydrous cobalt chloride. An immediate reaction occurred heat being formed and a dark black material separated out. The ether solution on standing for some minutes became quite clear and green and this green colour was attributed to cobalt chloride which is of course soluble in ether but insoluble in benzene. Some a-dinaphthyl was found in the ether solution by pouring into water and evaporating the ether. This a-dinaphthyl could have arisen

from the decomposition of an organic cobalt compound but some biradical formation also occurs in the formation of Grignard compounds themselves.

Attention was next centred on the dark black oily residue or precipitate. This was examined by extraction with solvents and by treating with water, etc. but most information was gained by study of a benzene extract. When dry benzene was added to the residue a green colouration was at first evident but this was almost immediately replaced by a pink colour. This pink colour was found to be caused by iodine. Examination of the benzene extract further revealed the presence of cobalt and a solid nitration product was also obtained. The nitro derivative melted at 64° and thus appeared to be a mixed nitro derivative of some hydrocarbon other than benzene, possibly naphthalene.

It was evident that the black residue could contain a mixture of a large variety of compounds among which were probably dinaphthyl, cobalt chloride, magnesium iodide and chloride, and others. The difficulty of isolating from such a mixture any possible organo-cobalt compounds was at once evident. The first attempt at a solution of this problem consisted of the preparation of some of the black residue, the extraction of this residue with ether and then the analysis of this ether solution. It was realised that the residue was formed in ether solution and should therefore be

rather insoluble in ether but some solubility in ether was noted and this seemed to be the best solvent at hand.

10 grams of a-naphthyl bromide were treated with 1 gram of magnesium to form the Grignard reagent and to this solution was then added excess of solid cobalt chloride. The residue formed and an ether extract was obtained by standing with ether overnight. Aliquots of this ether solution were analysed and the results are set out below.

Cobalt	.0052 grams/10 mls.
Organic material	.0267 "
Bromine	.0109 "
Chlorine	.0128 "
Magnesium	.0095 "

The organic material was found by removing the ether in hot water and weighing the residue. Interpretation of these results is obviously impossible in view of the high proportions of magnesium and the halogens.

It was now hoped that clearer results might be obtained by using the very reactive thiophene as a starting point. Iodothiophene was therefore converted into thiophene magnesium iodide and treated with cobalt iodide.

5 grams iodothiophene and 0.6 grams magnesium were used to form the Grignard and then 4 grams of cobalt iodide was added. After the reaction all the ether was removed under

reduced pressure and the residue extracted with benzene. The benzene extract was a yellow green colour and contained cobalt and iodine. When the benzene extract was treated with alcohol and mercuric chloride a blue colour developed which seemed to indicate that the mercury was replacing cobalt possibly from an organic cobalt compound.

The reactions employing a-naphthyl halides and cobalt halides were next repeated, a slightly modified technique being employed. Thus 20 grams of a-naphthyl bromide were treated with a slight excess of magnesium, 2.5 grams, to form the Grignard compound and the resulting ether solution was then reacted with a solution of cobalt halide in ether. When solutions of both Grignard reagent and of cobalt salt were used it was found that the reaction mixture was composed of two parts, an ether solution and an oily precipitate. The precipitate was of course a product of the reaction and was examined for the organo-cobalt compounds. All the excess cobalt halide was left in the ether while the Grignard reagent was all utilised in the reaction. In all experiments an excess of cobalt salt was used.

The a-naphthyl magnesium halide was prepared in about 100 mls. of ether and to this was added the ether solution of cobalt halide. The iodides and the bromides of cobalt were used as these were found more soluble in ether than the other cobalt halides. When the cobalt halide was added heat was

evolved and a dark green precipitate formed. After boiling the mixture for about 15 minutes to complete the reaction the mixture was allowed to settle and the ether decanted. As rapidly as possible to prevent the influx of air about 100 mls. of dry benzene was added and the mixture stood overnight. In this way the cold benzene extracted a considerable portion of the residue and became coloured green or blue depending on the halides used. The benzene extract was examined. The following results were obtained:-

The benzene extract was unstable and deposited green and blue amorphous solids on standing for about a week. Heating also decomposed the solution, a black tarry material being sometimes obtained and at others a green solid. It was found that treatment of the benzene extract with petrol ether and with dioxane precipitated solid materials which contained halogen and cobalt and were also partly organic. These materials were soluble in ether but insoluble in benzene and were so different from the material originally present in the benzene. These materials were decomposed by all aqueous solvents such as water and acids. When decomposition was effected with water cobalt hydroxide was formed and some cobalt halide but when acids were used cobalt halides were the only product. Silver nitrate also decomposed the compounds with the formation of silver halide and a method was thus

immediately available for the quantitative assay of these compounds for halogen and for the qualitative estimation of bromides and iodides.

A series of experiments was now carried out and these will be described in some detail.

20 grams of naphthalene halide was heated with 2 grams of magnesium to form the naphthyl magnesium halide. The final volume of the ether solution was about 100 mls. To prepare the Grignard compound it was necessary to heat the solution for about 2 hours as the naphthyl Grignard compounds are comparatively slowly formed. This ether solution was decanted and to the clear solution was added an ether solution of cobalt halide, an immediate reaction taking place. Cobalt halide was added to the reaction mixture until all signs of reaction were finished and excess cobalt halide was present. This was evident from the colour of the solution. At first the colour of the ether solution of cobalt halide was immediately dissipated but at the end of the reaction the colour was definitely established. Considerable heat was evolved and a dark green solid formed. The latter was oily and clung to the sides of the reaction flask. The mixture was heated for about 15 minutes to complete the reaction and when all the precipitate was settled out the ether was decanted and 100 mls. of dry benzene added, and the mixture stood overnight. The benzene became coloured green and was filtered

off. As heating of this benzene extract deposited a mixture of solids of varying composition and was furthermore attended by considerable decomposition some other method of isolating the compounds had to be found. This was done by treating a portion of the benzene extract with petrol ether (b.p.40-60) and with dioxane. These two solvents precipitated solids from the benzene solution and these solids were next analysed.

It would perhaps be appropriate now to discuss the methods used to analyse these compounds. As has been mentioned the compounds under consideration are all decomposed by silver nitrate, and so the method used for the estimation of halogen in these compounds consisted briefly of decomposing a weighed sample in a known volume of standard silver nitrate and then back titrating the excess silver nitrate with standard potassium thiocyanate using ferric alum indicator.

Cobalt was estimated by heating a weighed sample in a porcelain crucible and then dissolving the residual cobalt oxide in hydrochloric acid and estimating in the usual way with a-nitroso b-naphthol. Fuller details of these methods are given later.

The results of the first group of reactions carried out are given below in a brief manner.

Examination of the benzene solution

(a) Precipitation with petrol ether.

When 10 mls. of the benzene extract were poured into 50 mls. of petrol ether a precipitate formed. This was filtered off and examined. From analysis the precipitate was generally of the type

$RCoX_3$ where R- : naphthyl radicle.

At times this precipitate seemed to be contaminated with halides of the type R_2CoX_2

(b) Precipitation with dioxane

When 10 mls. of benzene extract were treated with 50 mls. of dioxane a precipitate formed, generally of the type R_2CoX_2.

Reaction 1 (N.B. R always refers to naphthyl and X to halogen)

a R Mg Br + Co Br_2 → a RCo Br_3 + a R_2Co Br_2

(a) Precipitate with petrol ether.

Analysis		a RCo Br_3 requires	
Co	13.8%	Co	13.9
Br_2 Values	45.0-54.1%	Br_2	56.3

(b) Precipitate with dioxane

Analysis		a $R_2Co\ Br_2$ requires	
Co	10.8	Co	12.4
Br_2	33.7	Br_2	33.8

Reaction 2

$$a\ RMgBr + CoI_2 \rightarrow a\ RCoI_3 + a\ R_3CoI$$

(a) Precipitate with petrol ether

Analysis		a $RCoI_3$ requires	
Co	10.2	Co	10.3
I_2	68.2	I_2	67.5

(b) Precipitate with dioxane

Analysis		a R_3CoI requires	
Co	10.8	Co	10.3
I_2	22.1	I_2	22.4

Reaction 3

$$b\ RMgBr + CoBr_2 \rightarrow b\ RCoBr_3 + b\ R_2CoBr_2$$

(a) Precipitate with petrol ether

Analysis		b $RCoBr_3$ requires	
Co	15.2	Co	13.9
Br_2	44.0	Br_2	56.3

(b) Precipitate with dioxane

Analysis		b R_2CoBr_2 requires	
Co	-	Co	-
Br_2	31.2	Br_2	33.8

N.B. Cobalt values not yet obtained.

Reaction 4

$$a\ RMgI + CoI_2 \rightarrow a\ RCoI_3 + a\ R_2CoI_2$$

(a) Precipitate with petrol ether

Analysis		a $RCoI_3$ requires	
Co	12.0	Co	10.3
I_2	65.0	I_2	67.5

(b) Precipitate with dioxane

Analysis		a R_2CoI_2 requires	
Co	11.6	Co	10.3
I_2	44.5	I_2	44.8

Reaction 5

$$a\ RMgI + CoBr_2 \rightarrow a\ RCoI_3 + a\ R_2CoI_2$$

This experiment was carried out to determine whether the organo metallic iodide or bromide was formed.

The precipitate with petrol ether contained 66.2% iodine and the iodine was checked chemically. The precipitate gave silver iodide with silver nitrate insoluble

in concentrated ammonia, and also characteristic violet iodine vapours with sulphuric acid. It was also established chemically that the precipitate with dioxane contained iodide and not bromide. Thus this reaction yields the organo metallic iodides, only the compound $RCoI_3$ having been definitely characterised.

At this stage in the work an experiment was performed using phenyl halides instead of the naphthyl halides and it was found that the reaction also occurred in this case. The analytical results were however much more difficult to interpret, and these are set out below.

20 grams of phenyl bromide was treated with magnesium to form the phenylmagnesium bromide and to the solution of this compound in ether was added excess of an ethereal solution of cobalt bromide. An immediate reaction occurred and a dark precipitate formed with the evolution of heat. The excess ether was decanted and dry benzene added to the residue and this benzene extract was then treated in the usual way. With petrol ether and dioxane blue precipitates formed and these were analysed for cobalt and halogen in the usual manner. By igniting a portion of the materials and weighing the residues and then estimating the percentage of cobalt in the ash it was found that in this experiment a significant amount of magnesium was present which was calculated by difference.

Petrol ether precipitate		Dioxane precipitate
% cobalt	5.5	2.8
% bromine	55.0	38.0
% magnesium	10.7	4.9

It is immediately evident that the percentage of magnesium is so high relative to cobalt that an accurate formulation from these results is virtually impossible. In the previous experiments with naphthyl halides the compounds obtained were tested for magnesium and only traces were found. However an experiment was designed to try and eliminate the presence of the magnesium. The obvious explanation of the presence of magnesium seems to be that the organo-cobalt compounds are formed by adding an ethereal solution of cobalt halide to an ethereal solution of the Grignard reagent and thus it seems likely that the precipitate which forms would tend to occlude some of the solution in which the precipitation was being carried out or at least of the materials present in that solution. Thus in this case it would be the magnesium Grignard compound which would be the impurity. It was resolved therefore to reverse the order in which the ethereal solutions were added to each other. Thus an experiment in which the Grignard reagent was added to the cobalt halide solution was performed. Obviously in this

case/the reaction proceeds as the Grignard reagent must be used up as it is added and therefore since there is always an excess of the cobalt halide this latter material should be the impurity. As the precipitate forms it forms in cobalt halide and as this material is insoluble in benzene, which is the solvent used for the extraction, little cobalt halide should be found in the final product as an impurity.

An exactly similar experiment using phenyl halide was carried out but the ethereal solution of the Grignard reagent was added to the solution of the cobalt halide in ether. The results obtained by this method are shown below.

	Petrol ether precipitate	Dioxane precipitate
% cobalt	14.4	12.0
% bromine	51.5	36.5
% magnesium	0	0

And thus a precipitate free from magnesium has been formed. Similar experiments were next performed using naphthyl halides.

In an experiment in which the cobalt halide was added to the Grignard compound the results showed small but quite appreciable amounts of magnesium.

Petrol ether precipitate		Dioxane precipitate
% cobalt	10.2	8.9
% bromine	43.8	36.6
% magnesium	1.3	3.6

By using the other order for the addition of the ether solutions this magnesium impurity was quite eliminated.

One other important result was also noted in these experiments and it was that the yields were considerably higher. It was thus resolved to repeat the experiments, with naphthyl halides, using the new technique and paying careful attention to yields.

The results so far obtained may be briefly summarised as below.

1. The formation of organo-cobalt compounds has been attempted by the usual methods for the formation of organo metallics, and has been made finally by the decomposition of Grignard reagents. Other methods lead to biradicals possibly through the decomposition of some intermediate unstabl organo metallic compound of cobalt.

2. By decomposing naphthyl magnesium halides with cobaltou halides organo-cobalt compounds of the type $RCoX_3$ and R_2CoX_2 and R_3CoX have been formed the last of these in the iodide series only.

3. Yields of the compounds were very low, being in the region of 20% in reaction 2 but considerably less in the other cases examined: 5% and in the beta series less than 2%.

4. A most satisfactory method for the preparation of very pure organo-cobalt compounds has been devised. This method will be used in all later work.

(c) Account of a series of experiments using a- and b-naphthyl halides

Experimental method

20 grams of the naphthyl halide were treated with the theoretical amount of magnesium to form the naphthyl magnesium halide. Usually 2.0 - 2.3 grams of magnesium were required for this. The final volume of the ether solution was adjusted to 100 mls. and the formation of the Grignard reagent required about 2-3 hours' heating on a water bath. The formation of the Grignard reagent usually took place in about 95% yield judging from the amount of the magnesium remaining after completion of the experiment. This ether solution containing the naphthyl magnesium halide was decanted and slowly added to an ether solution of cobalt halide, the volume of the latter being usually about 200 - 300 mls. This ether solution was saturated with cobalt halide and care was taken to ensure

that an excess of the cobalt salt was present during reaction. The two solutions were mixed under reflux as heat was formed in the reaction. Immediately a dark green precipitate formed and the reaction was completed by boiling on a water bath for 15 minutes. The excess ether solution was then decanted and 100 mls. of dry benzene added immediately so that no air could enter the flask. The precipitate was now left in contact with the benzene overnight when the benzene became coloured. The mixture was next filtered and the benzene extract stored in a stoppered bottle in the dark. In this way solutions could be kept for almost a week with little decomposition.

The benzene extract was next examined as in previous experiments. 10 mls. of the benzene solution were treated with 50 mls. of either petrol ether or dioxane so that precipitation occurred. The precipitates were immediately filtered, dried and weighed and then analysed. The results of these experiments are summarised below.

EXPERIMENTAL RESULTS

No.	Reaction	Products isolated with		Residue	Reaction No.
		Petrol ether	Dioxane		
1.	$RMgI+CoI_2$	$RCoI_3$	R_2CoI_2	1.5 g.	1.
2.	$RMgI+CoBr_2$	$RCoI_3$	R_2CoI_2	2.8 g.	2.
3.	$RMgBr+CoI_2$	$RCoI_3$	R_2CoI_2	13.1 g.	3.
4.	$RMgBr+CoBr_2$	$RCoBr_3.R_2CoBr_2$	R_2CoBr_2	9.5 g.	4.

All the above experiments are in the a-naphthyl series and the analytical results are shown below.

Compound	Experimental Results		Theoretical Results
$RCoI_3$	% cobalt	10.1	10.3
	% iodine	68.0	67.5
R_2CoI_2	% cobalt	10.8	10.3
	% iodine	44.5	44.8
$RCoBr_3.R_2CoBr_2$	% cobalt	13.3	13.2
	% bromine	45.0	45.0
R_2C0Br_2	% cobalt	12.8	12.4
	% bromine	33.7	33.8

Reactions in the Beta Naphthyl Series

Reaction	Products isolated with		Residue	Reaction No.
	Petrol Ether	Dioxane		
$RMgI + CoI_2$	$RCoI_3$	R_2CoI_2	No value	5.
$RMgI + CoBr_2$	$RCoI_3$	R_2CoI_2	No value	6.
$RMgBr + CoI_2$	$RCoI_3$	R_2CoI_2	4.5 g.	7.
$RMgBr + CoBr_2$	$RCoBr_2.R_2CoBr_2$	R_2CoBr_2	6.7 g.	8.

Analytical Results

Compound	Experimental Results		Theoretical Results
$RCoI_3$	% cobalt	10.8	10.3
	% iodine	67.2	67.5
$RCoBr_3.R_2CoBr_2$	% cobalt	13.0	13.2
	% bromine	46.0	45.0
R_2CoBr_2	% cobalt	13.7	12.4
	% bromine	34.6	33.8
R_2CoI_2	% cobalt	11.4	10.3
	% iodine	44.7	44.8

Discussion of results

A complete series of reactions in the naphthalene group have been obtained. Two types of organo-cobalt compound have been found: $RCoI_3$, R_2CoI_2 where R- is either the a- or b-naphthyl group. It is apparent too that the iodine

has a predominating influence and governs the reaction product whenever it is present in the reaction. This point is discussed more fully later. In the iodide compounds both the tri and di-iodide compounds are well defined. In the bromide compounds however only the di-bromide has been definitely characterised. Petrol ether precipitates a compound which seems to consist, according to the analytical figures, of an equimolecular mixture of the tri and di-bromides. This material appears quite homogeneous and no efforts have been so far made to separate the compound into possible components. Such a separation might possibly be made by differing solubilities in ether or some other solvent.

The Residue

In all experiments to prepare organo-cobalt compounds a residue has been left after the benzene extraction. This residue has been examined and several products found in it. Cobalt halide has been shown by extraction of the residue with water. In the case of reaction between a-naphthyl magnesium bromide and cobalt iodide the products isolated are cobalt iodide and organic material. The residues were all allowed to dry in the air after extraction with solvent was complete. Extraction with ether removed a material which formed a picrate mp. 140°. The picrate of a-dinaphthyl has mp. 145°. The residue still remaining after extraction with both water

and ether contained cobalt to the extent of 53% of this residue. It thus appears possible that in the reaction or in the decomposition of organo-cobalt compounds some cobalt metal is formed. In one experiment between a naphthyl magnesium iodide and cobalt iodide the weight of residue left after benzene extraction was 1.5 grams and the weight of material extracted was 18 grams of organo-cobalt compound. In this case therefore most of the material deposited is the organo-cobalt material and the slight amount of residue left after removal of these compounds probably arose from decomposition of the organic-cobalt compounds.

Efficiency of the Reaction

Without knowing the exact mechanism of a reaction it is difficult to form a very accurate idea of the efficiency of the process. However if we assume the tri-halides to be the main reaction product then some calculation may be made of the reaction efficiency from the weight of the petrol ether precipitate. We then have $RMgX + CoX_2 \rightarrow RCoX_3$ in which one molecule of the Grignard reagent gives rise to one molecule of the tri-halide. This statement has been used in the following calculations of the reactions efficiencie The residue remaining and which is insoluble in benzene has been weighed and these weights are also listed.

Reaction No.	Reaction	Efficiency or Yield %	Wt. of Residue after Extraction
1.	a $RMgI+CoI_2$	60.0%	1.5 grams
2.	a $RMgI+CoBr_2$	2%	2.8 "
3.	a $RMgBr_2+CoI_2$	25%	13.1 "
4.	a $RMgBr+CoBr_2$	2%	9.5 "
5.	b $RMgI+CoI_2$	No values	
6.	b $RMgI+CoBr_2$	No values	
7.	b $RMgBr+CoI_2$	47%	4.5 grams
8.	b $RMgBr+CoBr_2$	9%	6.7 "

In reactions 5 and 6 difficulties were experienced in making the Grignard reagents and as the reaction did not occur to completion the yields of organo-cobalt compounds have no significance. They were in any case extremely low, being of the order of 1%.

It is evident that the efficiencies of these reactions vary between very wide limits. This variation is probably due to slight differences in the technique with the different experiments. Nevertheless some general conclusions may be drawn regarding the reaction efficiency. The reactions which lead to products having iodine in the final product, (1,2,3,7) give better yields than those reactions in which

bromine is the only halogen. It may be noted that in reaction No.2 only 10 grams of the a naphthyl halide were used as a starting product, i.e. half the normal amount, and this may account in some measure for the low values obtained for the reaction efficiency. The alpha compounds are formed in better yields than the corresponding beta compounds. This result is of course in accord with theory that the reactions in the b-naphthalene series are slower than those in the a-series, and less efficient. The exceptionally high yields in reactions 1 and 7 are most noteworthy. This reaction is evidently so efficient that even in the beta series a yield of almost 50% is obtained. This yield is of course not obtained when the Grignard reagent is treated with a solution of cobalt halide, the Grignard reagent remaining in excess all the time. It is essential to add the Grignard reagent to the cobalt halide.

Thus the conclusions which may be drawn from these considerations of reaction efficiencies are:-

1. The iodides are formed more easily than the corresponding bromides.
2. The reactions in the alpha naphthalene series are more efficient than those in the beta series.
3. High yields of some organo-cobalt compounds (up to 60%) may be obtained.

Further discussion of these reactions in the naphthyl series is to be found in later work. Other similar reactions are then discussed and a more detailed account of these naphthalene experiments is better left until later.

The yields of the di-naphthyl cobalt halides are worthy of some attention. No actual values have been obtained for the yields of the dibromides as these compounds showed a definite solubility in the dioxane used to precipitate them. In an experiment using 20 grams of a-naphthyl magnesium bromide reacting with excess cobalt iodide the total weight of di-naphthyl cobalt di-iodide isolated was 12.3 grams. This corresponds to a yield of 50% of theory. Too much weight should not be placed on these figures however as the optimum conditions for precipitation were not obtained. Furthermore, a reaction with the precipitant, dioxane, occurs in the isolation of the organo-cobalt dihalides.

(4) Reaction with other aryl and alkyl groups

The experiments just outlined were taken as a basis for the further investigation of reactions with the Grignard reagent and cobalt halides using other groups such as methyl, ethyl and phenyl, etc. It has been already mentioned how the experiments with phenyl and ethyl groups were found to give organo-cobalt compounds but that these materials when

analysed did not seem to agree with the general type formulae found in the naphthyl series, e.g. $RCoI_3$, R_2CoI_2. It was apparent that some other effect was playing a part in these experiments.

It was noted that while the empirical formulae calculated from the analytical figures did not agree with any comparatively simple type such as $RCoI_3$ etc., the ratio of cobalt to halide was almost the same when calculated from the experimental and from the theoretical results. The ratio was found by $\frac{\%\ \text{cobalt}}{\text{Atomic Wt.}} / \frac{\%\ \text{halide}}{\text{Atomic Wt. of halide}}$ and was thus a ratio of numbers of atoms. These figures for some of the different radicles used in these experiments are shown below.

Radicle	Ratio of cobalt to halide	
	From Experiment	From Theory
Methyl	0.353	0.333
Ethyl	0.366	"
Propyl	0.305	"
Isopropyl	0.295	"
Phenyl	0.382	"

This table shows that in all these compounds the ratio of halide to cobalt is approximately 3:1 and thus all the compounds must be of the type $RCoX_3$. The theoretical

values used in the table are all for compounds of the type $RCoX_3$. Since the empirical formulae do not however agree with this type of formulation the compounds must all contain some extra constituent. If, for example, some type of solvation was occurring then the empirical formula would be affected but the ratio of cobalt to halide would be unaffected

In one experiment using ethyl magnesium iodide the benzene extract was coloured green and in a few hours this benzene solution began to deposit green solid materials. This deposition was accompanied by some decomposition as shown by the appearance of free iodine but the extent of this decomposition did not seem to be very great. This green material was found to be of the organo-cobalt type and was filtered off and analysed.

Results

% cobalt	11.2
% iodine	55.3

The theoretical results for the possible types of organo-cobalt compounds in the ethyl series are shown below.

Compound	% Cobalt	% Iodine
$C_2H_5CoI_3$	12.6	81.2
$(C_2H_5)_2CoI_2$	16.1	68.2
$(C_2H_5)_3CoI$	21.7	46.7

It is evident that the green material deposited from the benzene solution cannot be any one of these compounds nor can it be a mixture of them and must therefore contain some solvent attached in some way. In this case the solvent must be benzene.

This conclusion was further tested by extracting some of the black residue from the reaction between the ethyl magnesium iodide and cobalt iodide with a-chloro naphthalene. This material was found to be a good solvent for the organo-cobalt compounds and since it had a high molecular weight was an excellent solvent for testing this problem of possible solvation.

Extraction yielded a dark green liquid and precipitation with petrol ether gave a green yellow solid. It was possible of course that the solvent used to precipitate these organo-cobalt compounds was in some way attaching itself to the organo-cobalt molecule and so causing the difficulty in interpreting the analytical results but the fact that simple deposition from the benzene extract also gave a material which seemed to be solvated, refuted this possibility. The green solid obtained from the a-chloro naphthalene extract with petrol ether was decomposed with water when it was found that cobaltous hydroxide was formed and also a small amount of a brown oil. This oil was extracted with ether and the ether then removed. A slight residual oil remained.

This oil possessed a smell like naphthalene and formed a picrate melting at 136° and was thus identified as a-chloro naphthalene. A mixed melting point was also made with the picrate of a-chloro naphthalene. This experiment furnished conclusive proof that the solvent used in extracting the organo-cobalt compounds must in some cases at least attach itself to the molecule. This attachment must furthermore be so strong as to be unaffected by precipitation by another liquid, or by washing with various solvents.

The results obtained in the case of the alkyl radicles were next examined in the light of this new evidence of solvation and the results are set out below.

Experiment No.1

Reactants. CH_3MgI; CoI_2

Solvent used for extraction. Benzene.

Precipitate with petrol ether			$CH_3CoI_3.2C_6H_6$ requires
Analysis:	% cobalt	9.9	cobalt 9.7
	% iodine	60.5	iodine 62.3

Precipitate with dioxane

Dioxane precipitated an oil, brown in colour which decomposed in water and formed cobalt hydroxide. The oil was an organo-cobalt compound and was probably of the type $(CH_3)_2CoI_2$ but could not be analysed.

Experiment No.2

Reactants. C_2H_5MgI; CoI_2

Solvent used in extraction. Benzene.

Precipitation with petrol ether			$C_2H_5CoI_3.2C_6H_6$ requires
Analysis:	% cobalt	10.5	cobalt ... 9.5
	% iodine	61.7	iodine ...60.9

Precipitate with dioxane

Dioxane again gave only an oil.

Experiment No.3

Reactants. nC_3H_7MgI; CoI_2

Solvent used for extraction. Benzene.

Precipitation with petrol ether			$nC_3H_7CoI_3.C_6H_6$ requires
Analysis:	% cobalt	9.4	cobalt ...10.2
	% iodine	66.3	iodine ...67.9

Precipitation with dioxane

Dioxane gave a brown oil.

Experiment No.4

Reactants. $isoC_3H_7MgI$; CoI_2

Solvent used for extraction. Benzene.

Precipitation with petrol ether			$isoC_3H_7CoI_3.C_6H_6$ requires
Analysis:	% cobalt	9.2	cobalt ...10.2
	% iodine	67.3	iodine ...67.9

Precipitation with dioxane

Dioxane gave a brown oil.

Experiment No.5

Reactants. C_6H_5MgBr; $CoBr_2$

Solvent used for extraction. Benzene.

Precipitation with petrol ether			$C_6H_5CoBr_3.C_6H_6$ requires
Analysis:	% cobalt	14.4	cobalt ... 13.0
	% bromine	51.8	bromine .. 52.8
Precipitation with dioxane			$(C_6H_5)_2CoBr_2.C_6H_6$ requires
Analysis:	% cobalt	12.0	cobalt ... 13.1
	% bromine	36.5	bromine .. 35.5

Experiment No.6

Reactants. C_2H_5MgI; CoI_2

Solvent used for extraction. a-chloro naphthalene.

Precipitation with petrol ether			$C_2H_5CoI_3.a\text{-}C_{10}H_7Cl$ requires
Analysis:	% cobalt	10.2	cobalt 9.3
	% iodine	60.2	iodine 60.3

Dioxane precipitated a brown oil which decomposed with water to give cobaltous hydroxide, a gas (possibly ethane or butane) and an oil (unidentified).

We thus see that when groups in the alkyl series are used in these experiments to prepare organo-cobalt compounds, the resulting molecule contains one or more

molecules of the solvent used in the extraction of the organo-cobalt compounds. Similarly the phenyl compounds precipitate with a molecule or solvent. The definite amount of this solvent attached to the molecule indicates that the solvent is not simply absorbed by the organo-cobalt material. The attached solvent does not wash away with petrol ether or dioxane and this too indicates that the forces linking the solvent to the organo-cobalt molecule are quite strong ones. It will be noted that the amount of solvent attached to the various molecules varies with the size of both the hydrocarbon group from which the organo-cobalt compound has been formed and too with the size of the solvent molecule itself. The following table of the different organic cobalt compounds and the nature and number of solvent molecules illustrates this point.

Organo-cobalt Compound	Solvent	Number of attached molecules
$MeCoI_3$	Benzene	2
$EtCoI_3$	"	2
$nPrCoI_3$	"	I
$iPrCoI_3$	"	I
$EtCoI_3$	a-chloro naphthalene	I
$PhCoBr_3$	Benzene	I
Ph_2CoBr_2	"	I
$RCoI_3$	"	0
R_2CoI_2	"	0

R- as used in the last two types of organo-cobalt compounds is intended to signify either a- or b-naphthyl groups.

It is quite evident that possibly the main factor in determining the number of solvent molecules attached to an organo-cobalt molecule is the steric effect. Thus as the alkyl groups become larger from methyl to propyl the number of attached benzene molecules decreases from two to one. With the phenyl group, a comparatively large one, only one benzene molecule is attached, while the naphthyl group is so large as to prevent entirely the attachment of any solvent group whatever.

It is interesting to note too that while the compound $EtCoI_3$ can accommodate two benzene molecules only one of the larger a-chloro naphthalene molecules can be attached. Only two factors can determine the number of solvent molecules in any organo-cobalt compound and they are:-

1. The electronic distribution in the organo-cobalt compound.
2. Steric effects of the size of
   (a) solvent molecules.
   (b) The hydrocarbon group from which the organo-cobalt compound is formed.

Evidently steric effects play by far the most important part.

Mention might be made finally of the organo-platinum compounds. These are formed in the methyl series and have the form $(CH_3)_3PtI$. They are formed

in benzene solution and recrystallised from this solvent. No solvent attached to the compound has been found or reported in this case and this lack of solvent is probably due to the fact that the compound has three methyl groups around it and these would prevent by steric hindrance any solvent molecule attaching itself to the molecule.

Efficiency of the Reactions with Alkyl Groups & Phenyl Groups

Reaction	Product	Yield obtained
$MeMgI + CoI_2$	$MeCoI_3.2C_6H_6$	4%
$EtMgI + CoI_2$	$EtCoI_3.2C_6H_6$	4%
$EtMg + CoI_2$	$EtCoI_3.a\text{-}C_{10}H_7Cl$	36%
$nPrMgI + CoI_2$	$nPrCoI_3.C_6H_6$	8%
$iPrMgI + CoI_2$	$iPrCoI_3.C_6H_6$	8%
$PhMgBr + CoBr_2$	$PhCoBr_3.C_6H_6$	4%

It is evident from the above results that the efficiencies of these reactions are much lower than in the naphthalene series. The yields are all very close in all these cases and the only exception is the compound obtained when a-chloro naphthalene was used as an extractant. This material is evidently much more efficient as a solvent than benzene and its use could probably be extended to the extraction of other organo-cobalt compounds.

Extractants

Benzene is a satisfactory solvent for the organo-cobalt compounds. Other materials have been tried. Toluene and xylene as one might expect are both good solvents while cyclohexane does not extract any material whatever. The remarkable efficiency of a-chloro naphthalene noted above is probably due to two factors:-

1. a-chloro naphthalene contains halogen and this establishes similarity with the organo-cobalt compounds. Benzene and other hydrocarbons which do not contain halogen cannot do this.

2. Benzene, toluene, a-chloro naphthalene, etc. are all unsaturated whereas cyclohexane, similar to these aromatic compounds in nearly all respects except that of unsaturation, does not extract these organo-cobalt compounds at all. This establishes the importance of the unsaturated nature of the solvent. This also indicates that the organo-cobalt compounds may be like their solvents "unsaturated". This condition of unsaturation could exist in the organo-cobalt compounds if a type of resonance as occurs with the cobalt nickel carbonyls (See later, Electronic Configuration of Organic Cobalt Compounds) was also present in the cobalt compounds. This point must await magnetic studies however before it can be definitely solved.

(d) Reaction with other Group VIII elements

Very few organo-metallic compounds of the Group VIII elements have been described. Job and Reich[5] claim to have prepared ethyl iron chloride from ethylzinc iodide and ferrous chloride and the same product is obtained from the ferric chloride which is apparently first reduced to the ferrous state. The chief evidence in support of the iron compounds is that hydrolysis yields ferrous hydroxide. Champetier[6] prepared phenyl iron iodide as $2FeI_2 + 2PhZnCl \rightarrow 2PhFeI + ZnCl_2 + ZnI_2$

When iron halides are treated with the Grignard reagents the reaction yields mainly the coupling product. Gilman[7] obtained almost quantitative yields of biphenyl from reaction between phenylmagnesium iodide and the halides of the Group VIII metals. He found that lesser yields of biphenyl using osmium iridium and platinum were obtained, and suggested that the extent of coupling was a rough measure of the thermal instability of the intermediately formed organo-metallics and that the phenyl platinum compounds were most stable.

Pope and Peachey[8] have prepared the organo-platinum compounds by interaction of platinum chloride and methyl-magnesium iodide.

$$PtCl_4 + 3CH_3MgI \rightarrow (CH_3)_3PtI + 2MgCl_2 + MgI_2$$

It was later shown[9] that tetramethyl platinum was a byproduct in this reaction. The tetramethyl platinum has been easily prepared from trimethyl platinum iodide and methyl sodium.

$$(CH_3)_3PtI + CH_3Na \rightarrow (CH_3)_4Pt + NaI$$

By using the following reaction Gilman and Lichtenwalter have prepared hexa methyl di-platinum.

$$2(CH_3)PtI + 2K \rightarrow (CH_3)_3Pt\text{-}Pt(CH_3)_3 + 2KI$$

Powdered potassium was used in this experiment in dry benzene. Busch and Weber[10] have postulated organo-palladium compounds as intermediates in the catalytic reduction of aryl halides.

It was of some interest therefore to see how the method used successfully in the case of cobalt would serve in the case of the other Group VIII elements. Iron and nickel were chosen for this experiment. The two experiments carried out with these elements will be described in some detail.

Experiment with iron

a-naphthylmagnesium bromide was prepared and added to an ethereal solution of anhydrous ferrous iodide. As in the case with cobalt a reaction occurred and heat was evolved and a dark brown precipitate formed. This precipitate was

extracted with benzene overnight and a brown solution obtained. Materials precipitated from this extract with petrol ether and dioxane. These precipitates were brown in colour and were tested for halogen and iron. In this case iodide was found present but only magnesium was present as a metal and no iron could be found. The precipitates were analysed in the usual way and the results obtained are set out below. The magnesium figures were found simply by igniting and weighing the residue as magnesium oxide.

	Petrol ether precipitate	Dioxane precipitate
% Iodine	69.9	47.2
% Magnesium	5.0	4.8

$RMgI_3$ requires 71.4% iodine and 4.5% magnesium, while a-R_2MgI_2 requires 47.9% iodine and 4.5% magnesium.

Melting points

a-$RMgI_3$ melted at 160° and iodine was evolved at this temperature. a-R_2MgI_2 decomposed at 128°. Actually the compounds did not melt but rather decomposed.

Colour

Both these compounds were brown in colour.

Experiment with nickel

A solution of methylmagnesium iodide was prepared and added to solid anhydrous nickel chloride. An immediate

reaction occurred, heat was formed and a black precipitate formed. The ether in which the reaction was carried out was decanted and the black residue extracted with benzene. From this benzene extract petrol ether precipitated a pale yellow compound and dioxane gave an oil which contained iodine, and decomposed with water in the fashion of organo-cobalt compounds. The petrol ether precipitate analysed as follows:-

% iodine	57.9%
% magnesium	2.9%
$CH_3MgI_3.3C_6H_6$ requires iodine	58.2%
magnesium	3.6%

It was found that the petrol ether precipitate contained no nickel and that on ignition a white residue of magnesium remained. The magnesium was again estimated by washing and weighing as magnesium oxide. It is possible that better agreement with the magnesium figures could be obtained by decomposing the materials with acids and then estimating the magnesium as magnesium pyrophosphate.

It thus appears that this compound contains solvent combined in a similar manner to the solvent combined in some of the organo-cobalt compounds.

(f) Properties and reactions of the organo-cobalt compounds

Colour and solubility

The colours of the various organo-cobalt compounds are shown in the table below along with the solubilities in some of the more common solvents.

Compound	Colour	Solubility in Benzene	Ether	Petrol-ether	Dioxane	Chlorof.
$MeCoI_3$	Greenish yellow	i	s	i	sr	ss
$EtCoI_3$	"	i	s	i	sr	ss
$PrCoI_3$	"	i	s	i	sr	ss
$PhCoI_3$	"	i	s	i	sr	ss
a-$RCoI_3$	"	i	s	i	sr	ss
a-R_2CoI_2	Brown red	i	s	i	sr	ss
b-$R_3Co_2Br_5$	Blue	i	s	i	sr	ss
b-R_2CoBr_2	"	i	s	i	ss	ss

a-R- = alpha naphthyl; b-R refers to beta naphthyl.

a-R_2CoBr_2	Blue	i	s	i	ss	ss
a-$R_3Co_2Br_5$	"	i	s	i	sr	ss
b-$RCoI_3$	Yellow green	i	s	i	sr	ss
b-R_2CoI_2	Red brown	i	s	i	sr	ss

i = insoluble
s = definite solubility
ss = slight solubility
sr = soluble with reaction

From the table certain conclusions are evident. The colours of the organo-cobalt compounds fall into groups. Thus all the bromides are blue while the tri-iodides are green yellow in colour and the di-iodides a red brown. These differences in colour seem to be associated with the nature of the halide contained in the compound rather than with the hydrocarbon group.

All the organo-cobalt compounds are insoluble in benzene and this shows that the compounds under consideration are not identical with the original compound in the benzene extract from which they were obtained. Now an aliquot of the benzene extract from reaction of a-RMgI+CoI_2 was analysed for cobalt and for iodine and then the ratio of cobalt to iodine calculated. The value obtained was 0.383 and this indicates that the compound in the benzene extract contains CoI_3. Possibly some type of co-ordinative effect with the benzene renders the compound soluble at first. Whatever the actual reason may be the complex is easily broken as heating and solvent action cause the deposition of what may be called "secondary" organo-cobalt compounds. Even if the benzene extract is simply allowed to stand for a day precipitation of a benzene insoluble material begins.

The solubility of the organo-cobalt compounds in ether is most marked, green and blue solutions being obtained in the case of the iodides and bromides respectively.

The original compounds may sometimes be reprecipitated from the ether solution and a method of recrystallising is thus available. Thus $RCoI_3$ where R- is a-naphthyl gives a green solution in ether and one or two drops of dioxane will reprecipitate the original compound. Then too it has been noted that with the compounds derived from some of the lower groups such as ethyl, propyl, etc. dioxane precipitates a brown oil. This oil has been found soluble in ether. Precipitation from the ether can be made with dioxane but the brown solid which then precipitates in the case of the ethyl compounds contains iodine to the extent of only some 10.0% and thus cannot be a typical form of an organo-cobalt compound. In the example actually used the benzene extract contained $EtCoI_3.a\text{-}C_{10}H_7Cl$ and it appears that the oil which recrystallised from ether must contain ether attached to it. $(Et)_2CoI_2.a\text{-}C_{10}H_7Cl$ would contain 47.6% iodine. It is most probable that the di-iodide is first precipitated as an oil and that solution of this oil in ether removes the a-chloro naphthalene which is attached to the molecule and substitutes ether molecules. This point requires more investigation to verify this theory.

All the organo-cobalt compounds are insoluble in petrol ether and show only a slight solubility in chloroform. They show a definite solubility in dioxane but this is probably due to the reaction which dioxane initiates. This

point is discussed in much more detail later.

No actual measurements have been carried out on solubilities but in general the iodides are more soluble than the corresponding bromides.

Melting Points

The organo-cobalt compounds were all found to decompose at elevated temperatures without melting. The compounds were all placed in a narrow tube and vacuum applied when the tubes were sealed. Melting points were found by heating these sealed tubes. In general only a very gradual change was observed on heating. This change was a deepening in colour probably due to the formation of the cobalt halide. In some instances small amounts of violet iodine vapour were observed. In some cases it was possible only to place the decomposition temperature within a range of temperature.

Compound	Decomposition Point
$MeCoI_3.2C_6H_6$	140°
$EtCoI_3.2C_6H_6$	130°
$EtCoI_3.a\text{-}ClC_{10}H_7$	130-140°
$b\text{-}RCoI_3$	160°
$b\text{-}RC_2oI_2$	90°
$a\text{-}R_3Co_2Br_5$ CA	120°
$a\text{-}R_2CoBr_2$	"
$a\text{-}RCoI_3$	150-160°
$a\text{-}R_2CoI_2$	150-160°
$b\text{-}R_3Co_2Br_5$	150-160°
$b\text{-}R_2CoBr_2$	65°

Pyridine compounds

When to an ether solution of naphthyl cobalt tri-iodide pyridine was added a white flocculent solid was obtained. This material contained pyridine and was analysed.

Results		$RCoI_3.5Py$ requires
% cobalt	7.4	cobalt 6.2%
% iodine	39.4	iodine 39.6%

Comparison of the Halides

Certain observations may be made regarding the close similarity between the different halides in the organo-cobalt compounds. The iodides were always green or greenish yellow in colour while the bromides are generally blue. No specific reactions have been carried out to determine the relative reactivities of the compounds and so it is difficult to attribute any value to the differences in reaction rates of the organo-cobalt compounds caused by the differing halogens. Nevertheless it was observed that the iodides were much more unstable in the air and decomposed more quickly. The decomposition in air can be attributed to the action of the moisture in the air since a sample of a-dinaphthyl cobalt di-iodide in a sealed tube has kept for, at this time, two months, without the slightest visible trace of decomposition. The action of light does not seem to affect the materials in any way.

Reactivity of the Halides

Reaction between Grignard reagents and cobalt halides yields organo-cobalt compounds containing halogen. The nature of this halogen varies with the different experiments but certain consistent features are evident. Thus if either the Grignard reagent or the cobalt halide contains iodine then this iodine will appear in the final organo-cobalt compound. This conclusion is well illustrated in the examples given earlier and may be briefly sketched as below.

$$\left.\begin{array}{l} RMgBr + CoI_2 \\ RMgI + CoBr_2 \end{array}\right\rangle \longrightarrow RCoI_3 + R_2CoI_2$$

We thus see that in the above reactions the iodine replaces the bromine. Interaction between RMgI and nickel chloride also yields the iodine compound, this time a magnesium derivative. And so a similar conclusion may be reached concerning reaction between iodides and chlorides. Again in the reaction between RMgBr and ferrous iodide the resulting compound, a magnesium derivative, contains iodine and not bromine.

The normal order of replacement in the halogen series in ionic reactions is of course: F, CI, Br, I and so the expected replacement of iodine by bromine is not obtained.

Thus other factors appear to govern the reaction in this instance. This apparent abnormal behaviour may result from the ability of iodine to accommodate a decet of electrons and thus to confer greater stability upon the compound finally produced. However in view of the equal ease of formation of the bromides this does not appear to solve the problem.

It is interesting to note that two other reactions in the organo-metallic series also confirm this curious behaviour of the halides. The reactions of Pope and Peachey[8] for the preparation of the organo-platinum compounds involves reaction between methyl magnesium iodide and platinum chloride as:

$$PtCl_4 + 3CH_3MgI \rightarrow (CH_3)_3PtI + 2MgCl_2 + MgI_2$$

and here again we see the iodine present in the final reaction product, not chlorine.

Hein and co-workers[11] have studied the reaction between phenyl magnesium bromide and chromic chloride and isolated an organo-chromium compound containing bromine. All this evidence indicates that if the halides simply replace one another in these reactions then the correct order of replacement is I,Br,Cl,F. That is in reactions involving the decomposition of Grignard reagents with inorganic halides iodine replaces bromine, bromine chlorine and so on.

The reaction of Hein may be represented

$$5C_6H_5MgBr + 4CrCl_3 \rightarrow (C_6H_5)_5CrBr + 2MgBr_2 + 3MgCl_2 + 3CrCl_2$$

It is of interest in these considerations that studies of the relative stabilities of the bismuth compounds of the type $(C_6H_5)_3BiX_2$ where X is halogen have shown that the stabilities of the compounds are almost exactly in the order determined by the decomposition potentials of the potassium salts of the halogens in water: C,Cl,Br,I.[13] Thus the fluoride is most stable and a compound like $(Ph)_3BiI_2$ is extremely unstable. Now it has been already indicated that while no absolute measure of the stabilities of the organo-cobalt compounds have so far been obtained the iodides decompose more rapidly in the air(with water) than the bromides. It thus appears possible that halide governs the final product insofar as it is halide which determines the stability of the final compound. This conclusion may offer some guide to mechanism of the reaction.

Reactions of the Organo-cobalt Compounds

While no reactions for the determination of the relative stabilities of the organo-cobalt compounds have been made, several reactions of general interest have been investigated.

I. Reaction with dioxane

In an early experiment involving a-naphthyl magnesium bromide and cobalt iodide a precipitate was obtained with dioxane which when analysed showed a-R_3CoI where R is a a-naphthyl group. This experiment could not be repeated. In all later experiments dioxane precipitated the di-iodide of the composition a-R_2CoI_2. It was noticed that the dioxane actually reacted in the formation of the precipitate and some effort was made to examine this reaction.

A sample of a-$RCoI_3$(R= a-naphthyl) was treated with dioxane and some of the tri-iodide dissolved. The colour of the original tri-iodide changed from green to brown or red and in the dioxane solution iodine and cobalt iodide were found. The residue from this reaction when filtered off and analysed showed a-R_2CoI_2. This compound was an organo-cobalt compound and showed all the reactions of the, in this case, parent compound. Now the di-iodide also showed a definite reaction with dioxane. Further treatment with dioxane removed more iodine and cobalt iodide. As successive extraaqtions with dioxane were performed the iodine content of the product was examined.

These results are shown below.

No. of extractions	% Iodine in Compound
1.	44.8%
3.	33.4
6.	29.2
12.	24.2

All these materials contain approximately 10% cobalt and this value of course does not vary from a-$RCoI_3$ to a-R_3CoI. The mono-iodide contains 22.4% iodine theoretically and so this value has been nearly obtained. In one experiment a-$RCoI_3$ was boiled with dioxane approximately 250 mls. dioxane being used for 0.5 grams of the tri-iodide. This mixture was refluxed for 1 hour. The final product contained 38.8% iodine and so it appears that some other effect has been introduced in this case.

It is possible that the compound a-$RCoI_3$ tends to be in equilibrium as shown below and that given suitable conditions this equilibrium moves to the right.

$$a\text{-}2RCoI_3 \rightleftarrows a\text{-}R_2CoI_2 + CoI_2 + I_2 \qquad 1.$$

$$a\text{-}3R_2CoI_2 \rightleftarrows a\text{-}R_3CoI + CoI_2 + I_2 \qquad 2.$$

The reaction with dioxane seems to indicate the correctness of this mechanism. Thus both cobalt iodide and iodine have been shown in the dioxane solution. Also it has been found that 0.17 grams of a-$RCoI_3$ yield 0.096 grams of the compound a-R_2CoI_2 on treatment with dioxane. Theory requires the formation of 0.085 grams of the di-iodide, and this seems to offer further confirmation of the equilibrium as set out above.

A similar reaction probably occurs in the case of the bromides. This would account for the formation of the

formation of the a-R_2CoBr_2 with dioxane from the benzene extract. The lesser solubility of cobalt bromide in dioxane would tend to prevent the further formation of the compound R_3CoBr and the formation of this compound has not so far been observed.

Reaction with Water

All the organo-cobalt compounds decompose rapidly with water. Even if the compounds are allowed to remain in the air for a few minutes they absorb water from the air and decompose. The iodides are less stable than the bromides in this respect but both types decompose quickly. The reaction of the organo-cobalt compounds with water has been studied and certain products isolated from the decomposition. In all the samples decomposed with water, cobalt halide has been formed as the water contained soluble cobalt ions as shown by testing with 1-nitroso 2-naphthol. Cobalt hydroxide was also invariably formed and appeared as a blue solid. This blue solid turned brown in the presence of hydro-gen peroxide which is characteristic of cobalt hydroxide and on analysis this blue compound contained 62% cobalt.

In the case of the a-naphthyl cobalt tri- and di-iodides the ratio of cobalt iodide to cobalt hydroxide formed in decomposition with water has been determined. This was done by simply treating a sample of each compound with water

and filtering off the cobalt hydroxide. All the cobalt halide was of course soluble and by washing the precipitate with ether and alcohol all organic material was removed. The residue remaining was weighed as cobaltous hydroxide and from the amount of cobalt in the original sample the ratio of cobalt hydroxide to cobalt iodide was found. $RCoI_3$ decomposed with water. The cobalt was found as:

16.1% $Co(OH)_2$; 83.9% CoI_2

R_2CoI_2 gave 63.2% $Co(OH)_2$; 36.8% CoI_2

These results indicate that the decomposition varies between the two different compounds.

On decomposition with water all the organo-cobalt compounds formed an organic material. It is evident that the hydrocarbon group attached to the cobalt could react to form a variety of compounds. Thus the R-group which was in the cases tested a- or b-naphthyl, could couple to form di-naphthyl, disproportionate to give naphthalene and a variety of compounds of the tri-naphthyl type, or react with the solvent in which case naphthalene and naphthols could result. The melting points of some of these compounds and their picrates are shown below.

Compound	M.P.	M.P. of picrate
Naphthalene	80	149
α Dinaphthyl	160	145
a-naphthol	95	189
b-naphthol	122	156
b-dinaphthyl	188	184

A series of organo-cobalt compounds was decomposed with water and from this an ether extract obtained. This ether extract was found to contain the organic material formed in the decomposition. The ether was removed and the white organic residue dissolved in alcohol and a picrate formed by adding a saturated solution of picric acid in 95% alcohol and heating. The yellow picrates which separated out were filtered and dried. Sometimes separation of the picrate was made by centrifuging. The melting points of the picrates for the various organo-cobalt compounds are shown below.

Organo-cobalt Compound decomposed with water	M.P. of Picrate
a-$RCoI_3$	143
a-R_2CoI_2	112
a-$R_3Co_2Br_5$	115
a-R_2CoBr_2	105
b-$RCoI_3$	155
b-R_2CoI_2	150
b-$R_3Co_2Br_5$	142
b-R_2CoBr_2	153

It is immediately evident from these results that the organic material obtained by decomposition of the organo-cobalt compound with water is a mixture of substances. This conclusion is further supported by the fact that decomposition of a-$RCoI_3$ in water gave an organic material which melted at 140°. After twice recrystallising from alcohol the substance melted at 158°. Decomposition of b-$RCoI_3$ with water also gave an organic material melting at 127°. An alcohol extract of this material melted at 133-138° and that portion of the substance least soluble in alcohol melted at 145-155°.

Thus the conclusions which may be drawn from this evidence are:-

1. All the organo-cobalt compounds contain organic matter and on decomposition with water a mixture of organic substances is formed.

2. The organic material formed by decomposition forms picrates and is thus probably of naphthalene origin. The material is most likely to be di-naphthyl with some naphthalene.

Decomposition of such organo-cobalt compounds as $MeCoI_3$, $EtCoI_3$ etc. were all characteristed by the evolution of a gas. Ethane, butane, etc. could be formed by the decomposition of these organo-cobalt compounds in water.

3. Reaction with Sodium and Potassium

As has already been indicated the organo-cobalt compounds are all insoluble in benzene although the parent

material from which they are all precipitated is soluble in benzene. It was hoped to prepare a benzene soluble material by treating the organo-cobalt compound with sodium or potassium in the hope of removing iodine and thus increasing the proportion of the aryl group. Thus a compound of the type R_2-Co-Co-R_2 might result from the removal of iodine. Ether solutions of a-naphthyl cobalt tri-iodide were thus made and sodium and potassium added. No reaction could be induced however even by heating. Even the use of powdered potassium was unsuccessful. Some chance of success might be obtained by reacting the compound in liquid ammonia as this type of reaction has been used to prepare diphenyl germanium (14)

$(Ph)_2GeX_2 + 2Na \rightarrow (Ph)_2Ge \rightarrow ((Ph)_2Ge)_4$.

(g) General Theory

Reaction between Grignard reagents and cobalt halides has been shown to yield a precipitate containing organo-cobalt compounds. The organo-cobalt compounds are soluble in benzene, toluene and a-chloro naphthalene. The primary product of the reaction is probably the tri-halide. Some evidence is available in support of this. Analysis of a benzene extract in an experiment involving a-naphthyl magnesium bromide and cobalt iodide showed that the cobalt to iodine ratio was 0.383 and thus the compound in the benzene may be a-$RCoI_3$. The high yields of the tri-iodide obtained in some experiments (up to 60%)

again supports the idea that it is the tri-iodide that is the primary reaction product. However reaction with dioxane shows that a type of equilibrium between two types of organo-cobalt compounds, the tri-iodide and the di-iodide, is possible. This equilibrium is disturbed by dioxane so that the di-iodide is formed irreversibly. Reactions in which the organo-cobalt compounds containing bromine are formed may indicate that both the tri-and di-iodides are formed. Thus in the reaction between a-naphthyl magnesium bromide and cobalt bromide, petrol ether precipitates a compund which analyses correctly for an equimolecular mixture of the tri and di-bromides. It is thus possible that both compounds are formed in this reaction and that the two compounds are precipitated together. However it is possible that an equilibrium as shown below may obtained in the benzene solution and that under various conditions either the tri-iodide or an equimolecular mixture of the tri- and di-iodide may precipitate

$$2RCoX_3 = R_2CoX_2 + CoX_2 + X_2$$

Electronic configuration of the organo-cobalt compounds

Some comparison of the organo-cobalt compounds with the cobalt carbonyls seems possible. The carbonyls of the elements iron cobalt and nickel form a group with very similar electronic configurations.(35) Electron diffraction studies on nickel tetra carbonyl lead to the postulation of a resonating

electronic structure including the double bonded ideal -Ni:C:O. Similar considerations apply to cobalt nitroso carbonyl $Co(CO)_3NO$, and cobalt carbonyl hydride $Co(CO)_3COH$ which were shown to have tetrahedral structures with carbon to oxygen distances intermediate between those due to double and treble bonds and carbon to cobalt distances intermediate between those due to single and double bonds. The latter type of compound is best formulated as $H\ Co(CO)_4$ which accounts for a fairly stable potassium salt $K\ Co(CO)_4$.

Pauling[34] has deduced from spectroscopic and quantum mechanical considerations that elements in the iron group should obey the rules:-

1. Bond eigenfunctions should be formed from the nine eigenfunctions $3d^5$, 4s and $4p^3$ and one bond eigenfunction should be needed for each electron pair bond.
2. The remaining unshared electrons should be introduced into the 3d eigenfunctions not involved in bond formation.
3. The normal state should correspond to the state with the maximum resultant spin S allowed by the Pauli principle.

The only way to visualise the electronic structure of the cobalt tetracarbonyl anion is to use four: 3d, 4s and 4p orbitals for carbon to cobalt double bonds leaving a pair of unshared electrons in the remaining 3d orbital and an integral negative charge in the complex. The so called cobalt tetracarbonyl is dimeric indicating a covalent linkage through

the last available 3d orbital. Since nickel has one electron more than cobalt the absence of the anionic nickel tetracarbonyl and the monomeric form of nickel tetracarbonyl itself fit in with this type of electronic arrangement.

Neither magnetic measurements nor conductivity measurements have been so far made on the organo-cobalt compounds and it is thus impossible to say definitely what the electronic structure of these compounds is but the triiodides if monomeric should have one free electron with resulting paramagnetism. The dimeric form would of course be dimagnetic. A structure of tervalent cobalt surrounded with a quinonoid naphthyl group doubly bound, one doubly bound iodine with a decet and two covalent iodine linkages would require 3d and 4s orbitals only and would lead to a dimagnetic structure with resonance equalising the different cobalt to iodine bonds.

Possibly the most important problem immediately is whether the compounds of the type R_2CoX_2 have a planar or a tetrahedral configuration and thus whether isomers of this compound are possible. It seems likely that an experimental or empirical approach to this problem will yield results most easily.

(h) Summary and Conclusions

1. A number of methods have been investigated for the preparation of organo-cobalt compounds which have been finally prepared by the reaction of Grignard reagents with anhydrous cobalt halides.

2. The organo-cobalt compounds are of the type $RCoX_3$ and R_2CoX_2 where R is a hydrocarbon group, methyl, ethyl, propyl, naphthyl, etc., and X is halide as iodine or bromine. The reaction with the Grignard reagent appears to yield mainly the tri-iodides while the di-iodide types may be considered to result from reaction with dioxane.

3. The properties and some of the reactions of these compounds have been considered and some attention paid to the probable electronic configuration of the organo-cobalt compounds.

4. Reaction of Grignard reagents with iron and nickel has been studied and magnesium compounds of the type $RMgX_3$ and R_2MgX_2 (where R = a-naphthyl X = halide) have been isolated as products of the reaction.

(j) Experimental Methods

The following sub-section contains accounts of the methods of analysis used in the analyses of the organo-cobalt compounds and also the preparations of the materials used in this investigation.

Estimation of cobalt

The cobalt in the organo-cobalt compounds was estimated by two different methods both of which were found satisfactory.

Method 1

A sample of about 0.1-0.2 grams of the organo-cobalt compound was ignited in a porcelain crucible at red heat until all the organic material and the iodine or other halogen removed. The ash was then weighed as Co_3O_4. This ash of

cobalt oxide was then dissolved in 25 mls. of concentrated hydrochloric acid by heating until complete solution had taken place. The solution was evaporated to a volume of a few mls. and then diluted with about 25 mls. of water. This solution was then analysed for cobalt using 1-nitroso 2-naphthol in the manner described later.

Method 2

A sample of 0.1-0.2 grams of organo-cobalt compound was added directly to a solution of 25 mls. of concentrated hydrochloric acid. Decomposition occurred immediately and the cobalt went into solution. The solution was then filtered where necessary, to remove organic material and the solution then evaporated to dryness. The residue of cobalt chloride then remaining was dissolved in about 25 mls. of water containing 2 mls. of concentrated hydrochloric acid and the cobalt estimated with 1-nitroso 2-naphthol.

Estimation of cobalt with 1-nitroso 2-naphthol (15)

The weakly acid solution containing not more than 0.03 grams of cobalt was concentrated to 25 mls. and cooled. The cold solution was treated with 5 or 10 drops of 100 volume hydrogen peroxide and then 2N sodium hydroxide was added to precipitate the cobalt as cobaltic hydroxide. The beaker was kept covered during this operation. 10 to 20 mls.

of glacial acetic acid were then added and the mixture warmed gently to dissolve the precipitate. The solution was then diluted with boiling water to 200 mls. and about 20 mls. of freshly prepared 1-nitroso 2-naphthol added. About 0.25 grams of 1-nitroso 2-naphthol was needed for every 0.01 grams of cobalt. The solution was heated to gentle boiling until the precipitate coagulated and settled out. The supernatant liquor was tested for complete precipitation. The precipitate was filtered through a weighed Gooch crucible, washed with a little hot 33% acetic acid and then finally washed with hot water. The precipitate was dried to constant weight at 130° and weighed as $Co(C_{10}H_6O_2N)_3 2H_2O$.

Estimation of Halide

The halide in the organo-cobalt compounds was estimated very simply by the Volhard method. A sample of 0.1-0.2 grams of the organo-cobalt compound was added to 20 mls. of standard silver nitrate. The mixture was stirred and heated slightly to ensure thorough reaction and to allow the silver halide to coagulate. The excess standard silver nitrate was then back titrated with standard 0.1 N potassium thiocyanate using ferric alum as indicator. The percentage halide in the original compound was found from the relations

$$1 \text{ Ml N } AgNO_3 = 0.07992 \text{ g. Br} = 0.1269 \text{ g. I}$$

Preparations

Cobalt metal

Cobalt metal was made from cobalt oxalate by heating this material in an atmosphere of hydrogen. A long glass tube was packed with the oxalate and the hydrogen allowed through at a rate of about one bubble per second. As the compound decomposed the carbon and oxygen were removed. After reaction the contents of the tube were taken and the grey metal powder separated from any unchanged oxalate.

Pyrophoric cobalt

This material was made by forming an aluminium alloy with cobalt and then treating this alloy with caustic soda when the aluminium dissolved leaving a dark cobalt residue. This cobalt was used in experiments with diphenyl iodonium iodide.

Metallic nickel and iron

These metal powders were made in the same way as cobalt powder. Thus the metal oxalates were decomposed in a stream of hydrogen in a red hot glass tube.

Metal halides

In work on the preparation of organo-cobalt compounds the halides, mainly the iodides and bromides, were

needed. These compounds were made in in the case of cobalt, nickel and iron. The metal hydroxides were first prepared generally by treating a sample of the chloride with sodium hydroxide. The hydroxides were then dissolved in the appropriate halogen acid and heated until the excess acid was removed. Further heating gave an anhydrous product. In all the experiments with Grignard reagents ether solutions of the metal halides were used and these ether solutions were of very high purity. In the case of the cobalt iodides and bromides the cobalt halide in the ether solution was 99% pure, as shown by analysis for halogen. The following compounds were made by this method:-

Cobalt bromide and iodide
Ferrous iodide
Nickelous bromide

Hydrobromic Acid

120 grams of KBr in 200 mls. of water was cooled in a large crock of water and ice and 90 mls. of concentrated sulphuric acid added at such a rate that the temperature did not exceed 75°C. After reaction was complete the mixture was filtered to remove potassium hydrogen sulphate and the filtrate distilled. The fraction of boiling point 126° was retained as 48% HBr. Yield 69 grams or 85% theory.

Hydrobromic acid was also prepared as a byproduct in the preparation of a-bromo naphthalene prepared by bromination of naphthalene in carbon tetra chloride.

Thiophene (Org. Syn. Col. Vol. II 578)

Phosphorus trisulphide was prepared by mixing the calculated amounts of phosphorus and sulphur in an earthenware pot, keeping the pot embedded in a sand pit. A match was applied to the mixture when a vigorous reaction ensued. After completion the pot was broken and the phosphorus trisulphide removed. This material was ground and used in the preparation of thiophene.

Sodium succinate was made by heating together caustic soda and succinic acid.

In a large retort 486 grams of anhydrous sodium succinate and 648 grams of phosphorus tri-sulphide were intimately mixed. The outlet of the retort was attached to a condenser and then the contents of the retort were heated over a flame. Reaction set in slowly and a yellow oil distilled and was condensed. This oil, thiophene, was dried over sodium hydroxide and sodium and fractionated. The yield of material boiling at 83-86° was 40 grams or 17% of the theoretical amount. Yields may have improved by using CO_2 to remove air from the retort before heating.

Iodothiophene (Org. Syn. Coll. Vol. II 357)

35 grams of thiophene were placed with 50 mls. of benzene in a wide mouthed glass bottle and cooled in ice water. With shaking and cooling when necessary 75 grams of yellow mercuric oxide and 109 grams of iodine were added over

a period of 20 minutes. The yellow mercuric oxide changed to crimson mercuric iodide. The mixture was filtered and the residue washed with three 25 ml. portions of ether. The ether benzene filtrate was shaken with sodium thiosulphate to remove excess iodine and then dried over 5 grams of calcium chloride. The ether and benzene were removed on a steam bath and the residue of iodothiophene was fractionally distilled under reduced pressure. The iodothiophene boiling at 73°/15 mms. was collected. Yield 63 grams or 72% theory.

a Bromonaphthalene (Org. Syn, Coll. Vol. I P.116)

In a 2 l flask 512 grams of naphthalene were placed with 170 mls. of carbon tetrachloride. The flask was equipped with a stirrer, a reflux condenser and a dropping funnel, the stem of which extended below the surface of the liquid.

The mixture was warmed on a steam bath to gentle boiling and 707 grams (220 mls.) of bromine was run in at such a rate that almost none of it was carried over with the hydrogen bromide out of the condenser. Twelve to fifteen hours was necessary for this operation and the mixture was constantly stirred on the steam bath until the evolution of HBr ceased (about 6 hours).

The mixture was next distilled from the steam bath under slightly reduced pressure until free of carbon tetrachloride; the residue was mixed with 20-30 grams of NaOH and

stirred at 90-100°C for 4 hours. The liquid was transferred to a flask for fractional distillation and distilled under reduced pressure. The foreruns contained much naphthalene and this was removed by chilling and filtering. The main fraction of bromonaphthalene passed over at 132-135°/12 mms. (145-148°/20 mms.) and a high boiling fraction of dibromonaphthalene was collected. The intermediate fractions and foreruns were systematically redistilled so that 600-620 grams pure bromonaphthalene (72-75% theory) and about 20 grams of dibromonaphthalene (mp. 60°) were obtained.

$$C_1OH_8 + Br_2 \longrightarrow a\ C_{10}H_7 + HBr$$

Diphenyl iodonium iodide (Org. Syn. V22. P.52)

The preparation of this material involved the following steps:-

1. $C_6H_5NH_2 + NaNO_2 + 2HCl \longrightarrow C_6H_5N_2Cl$

   $C_6H_5N_2Cl + KI \longrightarrow C_6H_5I$

2. $C_6H_5I + Cl_2 \longrightarrow C_6H_5\ I.\ Cl_2$

3. $C_6H_5ICI_2 + \underset{\text{steam}}{\xrightarrow{2NaOH}} C_6H_5IO + 2NaCl + H_2O$

4. $2C_6H_5IO \underset{\text{distillation}}{\longrightarrow} C_6H_5I + C_6H_5IO_2$

5. $C_6H_5IO + C_6H_5IO_2 \longrightarrow (C_6H_5)_2\ I.\ IO_3$

6. $(C_6H_5)_2\ I.\ IO_3 + KI \rightarrow (C_6H_5)_2\ I.I + KIO_3$

Reaction 1

100 grams aniline was diazotised in 100 mls. water and 480 mls. conc. HCl with 78 grams $NaNO_2$. Potassium iodide 90 grams was added and the mixture stood overnight. Later the mixture was heated until no more gas was evolved, cooled and stood until the heavy organic layer separated. The upper aqueous layer was siphoned off and NaOH (50 grams) added to the residue until the solution was alkaline. This was at once distilled. The last one-third of the steam distilled was collected separately and added to the aqueous layer from earlier portions of the distillate. This was acidified with conc. H_2SO_4 and again steam distilled. The iodobenzene from this operation was added to the main yield and dried over $CaCl_2$. The oil was distilled finally under reduced pressure. Yield 165 grams or 75% theory.

Reaction 2

In a flask protected from light and with a mechanical stirrer; inlet tube for introduction of chlorine, exit tube with a dry $CaCl_2$ were placed 150 mls. dry $CHCl_3$ and 102 grams (0.5 mol.) iodobenzene. The flask was cooled in an ice salt mixture and dry chlorine introduced as rapidly as absorption allowed until an excess was present. This required about 3 hours.

The yellow crystalline iodobenzene dichloride was filtered, washed sparingly with $CHCl_3$ and air dried.

Yield 125 grams or 90% theory.

Reaction 3

In a large mortar chilled in an ice bath were placed 55 grams (0.2 mole) of iodobenzene dichloride, 50 grams anhydrous Na_2CO_3 and 100 grams finely crushed ice. The mixture was ground thoroughly until all ice melted and a thick paste resulted. To this suppension was added 140 mls. 5N NaOH in 20 ml. portions with repeated trituration after each addition. Finally 100 mls. water was added to render the mixture more fluid and the mixture stood overnight. The product was collected and washed with suction.

Yield 34 grams or 76% theory.

Reaction 4

In a 5 l. flask 110 grams iodobenzene was made into a thick paste;with water the mixture was rapidly steam distilled until amost all the iodobenzene was removed. The flask was cooled and the white solid filtered and dried at room temperature.

The solid was washed with $CHCl_3$, again dried and finely ground.

Yield 55 grams iodoxybenzene or 93% theory.

Reactions 5 and 6

A mixture of 22 g. of iodosobenzene 24 g. iodoxybenzene and 200 mls. 1N NaOH were gently stirred with 1 l. of cold water and after settling the supernatant liquor of di-

phenyliodonium iodate was decanted through a filter. The solid residue was extracted twice with 50 ml. portions of water and the extracts decanted through the filter. An aqueous solution of 20 g. of KI was added to the combined filtrates:after the bulky white precipitate had stood for 2 hours it was filtered, washed with water and dried. Yield 30 g. 70% theory.

a-naphthyl iodide

The preparation of this material was found very difficult and several methods were tried, with only little success, for its preparation. The a-naphthyl iodide was finally prepared as were the b-naphthyl iodides and bromides, by reaction of the dinaphthyl mercury compounds with the appropriate halogen.

Method 1

Naphthalene 100 grams, iodine 100 grams were refluxed for 15 hours with 200 grams of sodium persulphate and 300 mls. of glacial acetic acid. This process is of course simply one of direct iodination. After refluxing the mixture was diluted with water but no oil was found to show the formation of a-naphthyl iodide.

Method 2

a-naphthalene 50 grams was diazotised in 34 mls. of water 312 mls. of concentrated hydrochloric acid, using 500 grams of ice for cooling. 50 grams of sodium nitrite was

added to the mixture. After the diazotisation was complete and the mixture stood for 30 minutes, 60 grams of potassium iodide was added and the mixture stood overnight. After boiling to complete the reaction the excess liquor was decanted when a small amount of a tarry material remained. By distilling this tar 10 grams of a-naphthyl iodide were obtained or 12% of theory. Better yields were obtained however by the method of reaction with the dinaphthyl mercury compounds.

b-naphthyl bromide

The preparation of this compound was attempted by the method of Oddo.(36) 14.3 grams of b-naphthylamine were suspended in 60 grams of hydrobromic acid (D I.19) and 50 grams of water. The mixture was cooled in ice to 5° when 7.3 grams of sodium nitrite in 40 mls. of water was added. After the diazotisation was complete a mixture of 36 grams of potassium bromide, 30 grams of copper powder and 100 grams of water were added. A reaction occurred and the mixture was left overnight. After boiling to complete reaction the mixture was steam distilled. The b-bromo naphthalene which came over was recrystallised from alcohol.

Yield .2 grams or 10% theory.

The yields in this preparation were thus very poor and better yields were later obtained by reaction of bromine with di-b-naphthyl mercury.

Di-a-naphthyl and di-b-naphthyl mercury (Org.Syn.Coll.Vol.II, 381)

This preparation is given for the b-naphthyl compounds but the reaction is exactly similar for the a-naphthyl compounds.

$$2C_{10}H_7N_2Cl.HgCl_2 + 6Cu \rightarrow (C_{10}H_7)_2Hg + 2N_2 + 6CuCl + Hg$$

In a 2 litre flask with a stirrer were placed 231 grams of the addition compound of b-naphthyl diazonium chloride and mercuric chloride. This was prepared by diazotising 143 grams of b-naphthyl amine in 450 mls. concentrated hydrochloric acid and 500 mls. of water with about 70 grams of sodium nitrite. After the diazotisation was complete the solution was filtered and a solution of 271 grams of mercuric chloride in 300 mls. of concentrated hydrochloric acid added slowly. Ice was added to keep the temperature at about 10°. A yellow precipitate separated and after stirring for about 30 minutes this precipitate was filtered off. This was sucked as dry as possible and then washed with water and acetone (300 mls.). The solid yellow compound was air dried to constant weight. Yield 380-390 grams or 80% theory.

To 231 grams of this yellow addition compound in 700 mls. of acetone 189 grams of copper powder were added. The mixture was cooled to 20° and stirred for one hour. 700 mls. of concentrated ammonia were then added, mixed well and stood overnight. The supernatant liquor was decanted and

the solid material remaining collected on a Buchner funnel. This solid was washed with 25 ml. portions of water, acetone and ether. After air drying the material was recrystallised from xylene using decolorising carbon. Yield 50 grams or 45% theory based on weight of the addition compound used.

From the dinaphthyl mercury compounds the bromides and iodides of both a- and b-naphthalene were prepared. The dinaphthyl mercury compound was dissolved in carbon disulphide and the calculated amount of halogen added. The flask was heated under reflux when the mercuric halide separated. After reaction was complete (usually in about 30 minutes) the mixture was filtered and the residue washed with carbon disulphide. The carbon disulphide was removed by evaporation and the residues remaining recrystallised from alcohol. The a-naphthyl iodide which was an oil was distilled.

Results

80 grams di-a-naphthyl mercury gave 67 grams a-naphthyl iodide or 80% theory.

30 grams of di-b-naphthyl mercury gave on treatment with iodine 24 grams of b-naphthyl iodide or 80% theory.

30 grams of di-b-naphthyl mercury gave on treatment with bromine 12 grams of b-naphthalene or 46% theory.

The a-naphthyl bromide was not prepared by this method.

Notes

1. Reagents used in the experiments with the Grignard reagents.

The ether used in the preparation of the Grignard reagents was purified by extraction with sodium permanganate and caustic soda. After washing with water the ether was dried over calcium chloride and then over sodium and finally distilled. The ether and other reagents such as benzene, petrol ether and dioxane, etc. were all kept over sodium so that complete dryness of all reagents was assured.

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